

**REMARKS**

This Amendment A is responsive to the first Office Action on the merits dated August 25, 2004. Applicants respectfully submit that claims 1, 2, 4, 5, 7-12, 14-19, 21-23, and 30 as set forth herein are in condition for allowance, and request allowance of claims 1, 2, 4, 5, 7-12, 14-19, 21-23, and 30 as set forth herein.

**The Status of the Claims**

Claims 1-24 have been substantively examined. Claims 25-29 have been withdrawn by the Examiner in response to a previous restriction.

Claims 1-24 stand rejected for certain deficiencies under 35 U.S.C. § 112, 2<sup>nd</sup> paragraph.

Claims 1-3, 19, 21, and 24 stand rejected under 35 U.S.C. § 102(e) as anticipated by Ninomiya et al., U.S. 6,083,575 (hereinafter "Ninomiya") or, in the alternative, these claims stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Ninomiya.

Claims 4-5, 18, and 22-23 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Ninomiya.

Claims 6-17 and 20 are indicated as containing potentially allowable subject matter.

**The references not found in the scanned USPTO file are supplied herewith**

Applicants include below a duplicate copy of the return postcard indicating receipt at the USPTO of the references on the June 7, 2002 IDS including 8 patent references, 4 foreign references, and 7 articles. Applicants include with this Amendment duplicate copies of the references and articles indicated in the Office Action as missing from the USPTO file, including: EP0568355, JP08179286, JP11153787, JP11237612, and the Kobayashi et al., Nazarenko et al., Corvazier et al., Jain et al., and Shimada articles.

RECEIVED COMMUNICATION DATED: May 30, 2002

IN: Kumar et al. U.S. Patent Application No. 10/070,396 entitled  
"FABRICATION OF ALIGNED LIQUID CELL/FILM BY  
SIMULTANEOUS ALIGNMENT AND PHASE SEPARATION"

Information Disclosure Statement

PTO Form 1449

8 U.S. patent references; 4 foreign references & 7 articles

RLW/JJC/cw



KSU.P0201

The 35 U.S.C. § 112 deficiencies have been addressed

Claim 1 has been amended to more clearly define the relationship between the applying of polarized light, the inducing of phase separation, and resultant phase separated and aligned structure.

Claims 4-6 has been amended to clarify that this claim limits the applying operation of claim 1, and to clarify the geometric arrangement of the light source, polarizer, and substrate.

Claims 7-13 have been amended to change "second substrate" to "substrate" in most places. These amendments obviate the ambiguity between the two substrates cited in the Office Action, and are also consistent with the specification.

Claim 14 has been amended to clarify that the thermal process is part of the inducing of phase separation.

Claim 16 has been amended to clarify that the epoxy and resin are components of the initial prepolymer.

Claim 19 has been amended to specify liquid crystal material, and to change the "phase separation" processes to

"polymerization" processes. This amendment is supported in the original specification at least at page 8 lines 19-28.

Claim 23 has been amended to depend from claim 22.

It is believed that these amendments obviate the cited 35 U.S.C. § 112, 2<sup>nd</sup> paragraph deficiencies. Accordingly, Applicants respectfully request that the rejections under 35 U.S.C. § 112, 2<sup>nd</sup> paragraph be withdrawn.

**Withdrawn claims 25-29 are canceled herein**

In the interest of expediting prosecution, withdrawn claims 25-29 are canceled herein. However, Applicants reserve the right to prosecute these claims in a subsequent continuation, continuation-in-part, or divisional application.

**Claims 1, 2, 4, 5, 7-12, 14-18 and 30 patentably distinguish  
over the cited references**

Claim 1 as set forth herein calls for a method for fabricating simultaneously a phase separated organic film with alignment. A mixture of liquid crystal, prepolymer and polarization-sensitive material is prepared and disposed on a substrate. A polarized light from a light source is applied to said mixture disposed on the substrate. Phase separation of said mixture is induced simultaneously during said applying step to form a separate layer of homogenously aligned liquid crystal material adjacent a separate and distinct layer of polymer and said polarization-sensitive material on said substrate. The inducing includes polymerizing the prepolymer to generate the polymer layer. The alignment of the phase separated liquid crystal layer is induced by alignment of the polymer and polarization-sensitive material layer caused by the simultaneously applying of the polarized light.

Ninomiya does not disclose or fairly suggest phase separation induced simultaneously during applying of polarized light to form a separate layer of homogenously aligned liquid

crystal material adjacent a separate and distinct layer of polymer and polarization-sensitive material.

Ninomiya relates to polymer dispersion type liquid crystals (PDLC) in which liquid crystals are dispersed in interstices of polymers of a three-dimensional structure. Ninomiya col. 1 lines 7-15). The PDLC forming method of Ninomiya produces a single layer of polymer with liquid crystals arranged in interstices of the polymer layer. In contrast, the method of claim 1 calls for forming a phase-separated composite organic film (PSCOF) including a layer of homogenously aligned liquid crystal material and a separate and distinct layer of polymer.

As noted in the background of the present application (page 2 lines 18-19), the method for forming PSCOF is similar to that used to form PDLC. Both methods typically involve forming a prepolymer mixture and causing polymerization that leads to phase separation of the liquid crystal from the polymer. However, in PDLC, phase separation conditions lead to a single layer of polymer with interstitial liquid crystals, whereas in PSCOF the phase separation conditions lead to separate layers of liquid crystal material and polymer material.

Claim 1 and the method of Ninomiya are similar in that both use polarized light to induce liquid crystal alignment during phase separation. However, the skilled artisan having Ninomiya at hand would have had no reasonable expectation of success in achieving alignment of a phase separated liquid crystal layer based on the alignment of interstitial liquid crystals disclosed in Ninomiya. Ninomiya's interstitial liquid crystals are surrounded by polymer, providing extensive contact area between for the polymer to induce liquid crystal alignment.

In contrast, there is much less contact area between the liquid crystal and polymer layers of claim 1. The reduced contact area would be expected to be substantially less effective in inducing homogenous alignment in the liquid crystal layer. Accordingly, the skilled artisan would be unlikely to be motivated by Ninomiya to attempt to achieve simultaneous liquid



crystal layer phase separation and alignment using polarized light, as called for in claim 1.

For at least the above reasons, it is respectfully submitted that claims 1, 2, 4, 5, 7-12, 14-18, and 30 as set forth herein patentably distinguish over the cited references. Accordingly, Applicants ask for allowance of claims 1, 2, 4, 5, 7-12, 14-18, and 30 as set forth herein.

**Claims 19 and 21-23 patentably distinguish over the cited references**

Claim 19 as set forth herein calls for a method for fabricating a liquid crystal device with alignment properties. A first mixture includes at least a first polarization-sensitive agent and a prepolymer. A second mixture includes at least a second polarization-sensitive agent and a prepolymer. A liquid crystal material is mixed into either the first or second mixture. The first mixture is disposed on a substrate, and the second mixture is disposed over the first mixture. A first polymerization process is applied to the first mixture, and a second polymerization process is applied to the second mixture. The first and second polymerization processes are each selected from the group consisting of (i) applying polarized visible light, (ii) applying polarized ultraviolet light, (iii) applying thermal induction, (iv) applying chemical induction, and (v) applying solvent induction. The polymerization processes cause the liquid crystal material to phase separate into a separate and distinct phase-separated liquid crystal layer. At least one of the first and second polymerization processes apply polarized visible or ultraviolet light that imparts orientational alignments to said liquid crystal layer.

Ninomiya does not disclose or fairly suggest polymerization processes that cause the liquid crystal layer to phase separate into a separate and distinct phase-separated liquid crystal layer. Ninomiya also does not disclose or fairly suggest at least one of first and second polymerization processes applying

polarized visible or ultraviolet light that imparts orientational alignments to said liquid crystal layer.

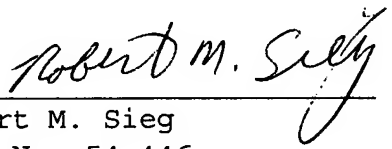
Moreover, the use of polarized light during phase separation in Ninomiya to induce alignment of liquid crystals positioned at interstices of a polymer layer does not make obvious the method of claim 19 which calls for aligning a separate and distinct liquid crystal layer during a polymerization process that includes applying polarized light. One skilled in the art would have no reasonable expectation, based on alignment of the interstitial liquid crystals in Ninomiya, that a separate and distinct phase-separated liquid crystal layer could be aligned by polarized light applied in phase separation.

**CONCLUSION**

Applicants respectfully submit that claims 1, 2, 4, 5, 7-12, 14-19, 21-23, and 30 as set forth herein are in condition for allowance, and therefore request allowance of claims 1, 2, 4, 5, 7-12, 14-19, 21-23, and 30 as set forth herein.

Respectfully submitted,

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Enclosures: EP0568355  
JP08179286  
JP11153787  
JP11237612  
Kobayashi et al. article  
Nazarenko et al. article  
Corvazier et al. article  
Jain et al. article  
Shimada article

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**A liquid crystal display device and a method for manufacturing the same.**

A liquid crystal display device of the present invention includes: two substrates facing each other, at least one of the substrates being transparent; electrodes disposed on inside surfaces of the respective substrates; a display medium which is provided between the two substrates and formed of polymer walls (17) containing a polymer as their main component and liquid crystal regions (16) containing liquid crystal as their main component; and a plurality of pixels, wherein the liquid crystal regions are partitioned by the polymer walls and are close to the substrates, portions of the liquid crystal regions close to the substrates being in parallel with the substrates, an interval  $a$  between the center of one liquid crystal region and the center of an adjacent liquid crystal region in a direction along the surface of the substrate is within a width of one pixel along the direction, and 80% or more of the intervals  $a$  satisfy the relationship:  $3b/2 > a > b/2$ , where  $b$  is an average of the intervals  $a$ .

**EP 0 568 355 A2**

**BACKGROUND OF THE INVENTION****1. Field of the Invention:**

5 The present invention relates to a liquid crystal display device in which a display medium having liquid crystal regions partitioned by polymer walls formed of a polymer is sandwiched between two facing substrates, and a method for producing the same.

**2. Description of the Related Art:**

10 There are various kinds of display modes for a liquid crystal display device. For example, as liquid crystal display devices taking advantage of electro-optic effects, liquid crystal display devices of a twisted nematic (TN) mode, a super twisted nematic (STN) mode, etc. using nematic liquid crystal molecules have been put to practical use. In addition, a liquid crystal display device using ferroelectric liquid crystal (FLC) has been proposed. These liquid crystal display devices require polarizing plates and an orientation treatment.

15 Examples of liquid crystal display devices taking advantage of light scattering of liquid crystal, requiring no polarizing plates include a liquid crystal display device of a dynamic scattering (DS) mode or a phase change (PC) mode.

20 In recent years, a liquid crystal display device requiring no polarizing plates or orientation treatment; i.e., a liquid crystal display device taking advantage of the birefringence of liquid crystal and electrically regulating a transparent state and an opaque state of the device has been proposed. According to the system of this type of liquid crystal display device, a display is performed as follows:

25 When liquid crystal molecules are aligned by the application of a voltage, the ordinary refractive index of the liquid crystal molecules and the refractive index of a medium for supporting the liquid crystal molecules, such as a polymer coincide with each other, whereby a transparent state is obtained. On the other hand, when no voltage is applied to the device, light scattering is caused due to the turbulence of the orientation of the liquid crystal molecules. In this way, a display is performed.

As a method for producing a light scattering type liquid crystal display device of this system, the following five methods have been proposed.

30 (1) A display medium is obtained by making liquid crystal contained in polymer capsules (Japanese National Publication No. 58-501631).

(2) A light-curable or thermosetting resin and liquid crystal are mixed; and only the resin is deposited and cured. Then, liquid crystal regions in a spherical shape are formed in the cured resin (Japanese National Publication No. 61-502128).

35 (3) The diameter of spherical liquid crystal regions is regulated (Japanese Laid-Open Patent Publication No. 3-72317).

(4) A polymer porous film is impregnated with liquid crystal (Japanese Laid-Open Patent Publication No. 3-59515).

40 (5) Beads formed of a polymer which become a source for light scattering are floated in liquid crystal provided between two transparent electrodes disposed apart from each other (Japanese Laid-Open Patent Publication No. 3-46621).

45 However, in the case of method (1), since the liquid crystal contained in the polymer capsule is in the form of an individual sphere, a drive voltage for changing the orientation of the liquid crystal molecules is varied depending upon each liquid crystal region. As a result, a drive voltage for simultaneously operating all of the liquid crystal regions is increased, narrowing the application range of the liquid crystal display device.

In the case of method (2), it is difficult to precisely regulate each diameter of the liquid crystal regions in a spherical shape although a phase separation method is used.

In the case of method (3), it is difficult to precisely align the liquid crystal regions in a round shape in a planar manner although a phase separation method is used.

50 In the case of method (4), there are advantages in that appropriate resin materials and liquid crystal can be selected over a wide range, since a phase separation is not utilized when the liquid crystal regions are formed; and polymer porous films can sufficiently be purified. However, there are disadvantages in that each diameter of the liquid crystal regions in a round shape cannot sufficiently be regulated; and the liquid crystal regions cannot precisely be positioned in a direction along the surface of the substrate.

55 In the case of method (5), although the intensity of light scattering is large, it is difficult to uniformly disperse the beads and to cause light scattering at almost the same level in each pixel, resulting in the likelihood of an uneven display.

As described above, in a polymer dispersed liquid crystal display device using polymer type liquid crystal,

in which liquid crystal regions are dispersed, it has been difficult to form the liquid crystal display regions in a uniform manner and to precisely regulate the position of the liquid crystal regions in a direction along the surface of the substrate. Thus, the liquid crystal regions have a variety of different diameters and the distribution thereof is not uniform. In addition, because of the difficulty in precisely positioning the liquid crystal regions, the drive voltage for each liquid crystal region is different. This results in a threshold value characteristic curve which is not steep and the drive voltage becomes relatively high. Moreover, a number of small liquid crystal regions having low light scattering ability are present, so that contrast in the resulting display is relatively low.

Since the shape of the liquid crystal regions is not uniform and it is difficult to regulate the position of the liquid crystal regions in a direction along the surface of the substrate, a large screen cannot be obtained under a high precision condition. Moreover, in the case where a simple matrix drive method, in which signals are turned on/off to obtain an average signal and a liquid crystal display device is driven by the average signal, is used for the polymer dispersed liquid crystal display device, a duty ratio (i.e., a ratio of time during which each signal is turned on) cannot be made large.

Furthermore, in the polymer dispersed liquid crystal display device, it is difficult to perform orientation treatment. The reason for this is described as follows:

An example of an orientation treatment method is proposed in Japanese Laid-Open Patent Publication No. 3-52843 and "Liquid crystal", Vol. 5, No. 5, p. 1477, (1989). According to this method, a magnetic field, an electric field, etc. are applied to a liquid crystal display device during a production stage while a polymer is formed by the polymerization. However, in this method, since the surface of the polymer is not directly subjected to an orientation treatment, the orientation regulating ability is weak. In addition, liquid crystal molecules are aligned only in one direction, so that this method cannot be applied to modes such as a TN mode and an STN mode, in which liquid crystal molecules should be aligned in different directions to each other along the facing sides of two substrates sandwiching the liquid crystal.

Another example of an orientation treatment method is described in "Extended Abstracts", p. 320 (The 17th Liquid Crystal Forum). According to this method, liquid crystal molecules are indirectly oriented via polymer walls formed on substrates which are subjected to an orientation treatment. However, in this method, it is impossible to prevent a polymer from remaining on the surface of an orientation film on the pixel electrodes, which makes it difficult to directly align liquid crystal molecules and remarkably decreases an orientation regulating ability in the same way as in the above-mentioned method. This causes serious practical problems in the use of a liquid crystal display device obtained by using this method.

Moreover, as described above, in a liquid crystal display device which uses ferroelectric liquid crystal, requiring polarizing plates and an orientation treatment, a smectic (SmC\*) phase is utilized for the purpose of causing spontaneous polarization. The regularity of this phase structure is closer to that of crystal, compared with that of a nematic phase, so that the smectic phase is weak against a physical shock. In order to solve this problem, it is considered that a physical shock is alleviated by dispersing ferroelectric liquid crystal in a polymer. However, this method is not put to practical use since it is difficult to perform an orientation treatment in the polymer.

Japanese Laid-Open Patent Publication Nos. 63-264721 and 264722 propose a method for aligning ferroelectric liquid crystal molecules in a polymer. According to this method, a polymer in which ferroelectric crystal is dispersed is formed on a film and is subjected to uniaxial stretching, whereby the ferroelectric liquid crystal molecules are aligned. However, in this method, since a number of interfaces between liquid crystal regions and the polymer walls are present in one pixel, linearly polarized light which is incident upon a liquid crystal display device is scattered and part of the light is depolarized. As a result, the opaque level of the liquid crystal display device is decreased, which causes deteriorated contrast. In the same way, this problem is caused in other display modes requiring polarizing plates, such as the TN mode, the STN mode, and the electrically controlled birefringence (ECB) mode.

Japanese Laid-Open Patent Publication Nos. 59-201021, 61-205920, and 3-192334 disclose that in order to provide shock resistance of an FLC, polymer walls are formed by photolithography on a substrate material subjected to an orientation treatment to form a cell, and then liquid crystal is injected into the cell. However, according to this method, independent liquid crystal areas cannot be formed and cell thickness cannot be regulated with precision.

As described above, it is difficult to conduct an orientation treatment simultaneously with dispersing a liquid crystal material in a polymer. Even though the orientation treatment can be conducted, contrast is remarkably decreased due to the depolarization caused by light scattered on the interfaces between the liquid crystal and the polymer. The reason why it is difficult to conduct the orientation treatment is that the polymer enters between the substrate and the liquid crystal when the liquid crystal is dispersed in the polymer. The light scattering caused on the interfaces between the liquid crystal and the polymer can be prevented by decreasing the interfaces between the liquid crystal in the pixels and the polymer as much as possible and by making at

least one liquid crystal region present in one pixel (i.e., regulating the position and size of the liquid crystal regions). However, at the present time, the liquid crystal regions are naturally formed (i.e., the liquid crystal regions are formed under the condition that the position and size thereof are not regulated). Moreover, a liquid crystal display device using FLC has the problem of low shock resistance as described above.

The liquid crystal display devices obtained by the above-mentioned five methods (1) to (5) are light scattering type devices, and thus, these devices cannot be applied to the non light scattering type liquid crystal display devices of a TN mode, an STN mode, an ECB mode, etc.

In addition, for example, Japanese Laid-Open Patent Publication No. 2-153318 discloses that display areas of a liquid crystal display device are limited in a polymer by using a photomask. According to this method, transparent portions cured by light irradiation and uncured portions covered with the photomask are divided while a voltage is applied between electrodes. Then, the photomask is removed, and the uncured portions are cured to form scattering portions. The display device thus obtained is manufactured in view of a display of an independent pattern. When an electrical field is applied to the device, the light scattering portions become transparent, whereby the entire cell becomes transparent. However, in this method, the shape of liquid crystal is not regulated by the photomask.

Japanese Laid-Open Patent Publication No. 59-226322 discloses that a mixture containing a polymer material and a liquid crystal material is dissolved in a solvent, and the solvent is removed from the obtained solution, whereby a phase separation is conducted between the polymer and the liquid crystal.

Furthermore, Japanese Laid-Open Patent Publication No. 2-116824 discloses a method for fixing liquid crystal regions on polymer walls in a liquid crystal display device. According to this method, a liquid crystal material and a polymerizable liquid crystalline compound having a liquid crystalline functional group attached to its side chain are dissolved in a solvent. Then, the solution thus obtained was coated onto the surface of a substrate. After that, the solvent is removed, whereby a phase separation is conducted between the liquid crystal material and the liquid crystalline polymer to fix the liquid crystal regions on the polymer walls.

In the case of the respective above-mentioned suggested methods, unreacted monomers or oligomers remain in the liquid crystal regions of the polymer dispersed liquid crystal display device. Due to these remaining substances, the viscosity of the liquid crystal is high. As a result, the response speed is low. In order to overcome this problem, Japanese Laid-Open Patent Publication Nos. 4-14015 and 4-168422 disclose the use of a resin material of a fluorine type for the purpose of decreasing the drive voltage and improving the electrical holding ratio. However, when a liquid crystal display device is manufactured by using a resin material of a fluorine type, the response speed  $\tau_r$  under an applied voltage is increased due to the presence of the fluorine atoms on the interfaces between the liquid crystal and the resin. In contrast, the response speed  $\tau_d$  under no applied voltage is decreased, since the driving force (interaction (orientation regulating ability) between the polymer material and the liquid crystal material) for making the liquid crystal return to the original state is weakened.

Examples of a material generally used as a liquid crystal material include cyanobiphenyl type materials and cyanopyrimidine type materials having a CN group in its molecule. Those materials are disclosed in Japanese Laid-Open Patent Publication Nos. 2-28284, 2-75688, 2-85822, and 2-272422 to 2-272424. However, this CN group is polarized, has strong reactivity, and facilitates the introduction of the impurities of the entire system into the liquid crystal material. Because of this, there is a problem that in the manufacturing process for a polymer dispersed liquid crystal display device which has a number of chances to come into contact with other compounds, the liquid crystal display device thus obtained cannot maintain a high electrical holding ratio (90% or more). Moreover, in the case where the polymerizable material contained in a mixture of the liquid crystal material and the polymerizable material is cured to cause a phase separation between the liquid crystal and the polymer, reactive sites of the liquid crystal and the polymerizable material coexist in the mixture, which damages the liquid crystal to remarkably decrease the electrical holding ratio.

Furthermore, in a method for causing a phase separation between the liquid crystal and the photosetting resin by curing the photosetting resin, it is easy to regulate the size of liquid crystal regions; however, an unreacted monomer remains in a display medium containing the liquid crystal and the resin, and the strength of the polymer walls formed of the resin is not sufficient. Thus, electro-optic characteristics of the obtained cell is varied due to thermal change. In addition, there is a problem in that the adhesion between the substrate and the polymer dispersed liquid crystal material is low, so that the polymer dispersed liquid crystal material is partially peeled off from the substrate due to the contraction of the resin.

## **SUMMARY OF THE INVENTION**

A liquid crystal display device of the present invention includes:  
two substrates facing each other, at least one of the substrates being transparent;

electrodes disposed on inside surfaces of the respective substrates;  
 a display medium which is provided between the two substrates and formed of polymer walls and liquid crystal regions partitioned by the polymer walls; and

5 a plurality of pixels,

wherein an interval  $a$  between a center of one liquid crystal region and a center of an adjacent liquid crystal region in a direction along a surface of the substrate is within a width of one pixel along the direction, and 80% or more of the intervals  $a$  satisfy the relationship:  $3b/2 > a > b/2$ , where  $b$  is an average of the intervals  $a$ .

10 In another aspect of the present invention, a method for manufacturing a liquid crystal display device having a plurality of pixels, includes the steps of:

providing a mixture containing a photopolymerizable compound and a liquid crystal material between a pair of substrates, two substrates facing each other, at least one of the substrates being transparent, electrodes being disposed on inside surfaces of the respective substrates; and

15 irradiating light to the mixture with a light intensity distribution in which light intensity of at least one portion of each pixel is 90% or less of a maximum illuminance in a circular area which corresponds to 10 times the pixel area and whose center is situated in a center of the pixel.

In one embodiment, a photomask having a pattern with regularity is placed on the transparent substrate, and light is irradiated through the photomask to the mixture provided between the substrates.

20 In another embodiment, the pattern with regularity is formed on the photomask, and the pattern covers 30% or more of at least each pixel.

In another embodiment, the pattern with regularity is formed on the photomask, a minimum repeating unit of the pattern has a size within a circle having a diameter in the range of  $1\text{ }\mu\text{m}$  to  $50\text{ }\mu\text{m}$ , and an interval between a center of one unit and a center of an adjacent unit is in the range of  $1\text{ }\mu\text{m}$  to  $50\text{ }\mu\text{m}$ .

25 In another embodiment, the photomask having a pattern with regularity is placed inside one of the substrates, and light is irradiated through the photomask to the mixture provided between the substrates.

In another embodiment, the pattern with regularity is formed on the photomask, and the pattern covers 30% or more of at least each pixel.

30 In another embodiment, the pattern with regularity is formed on the photomask, a minimum repeating unit of the pattern has a size within a circle having a diameter in the range of  $1\text{ }\mu\text{m}$  to  $50\text{ }\mu\text{m}$ , and an interval between a center of one unit and a center of an adjacent unit is in the range of  $1\text{ }\mu\text{m}$  to  $50\text{ }\mu\text{m}$ .

In another aspect of the present invention, a liquid crystal display device includes:

two substrates facing each other, at least one of the substrates being transparent, electrodes disposed on inside surfaces of the respective substrates; and

35 a display medium which is provided between the two substrates and formed of polymer walls containing a polymer as their main component and liquid crystal regions containing liquid crystal as their main component;

wherein the liquid crystal regions are partitioned by the polymer walls and are close to the substrates, portions of the liquid crystal regions close to the substrates being in parallel with the substrates.

40 In one embodiment, an orientation direction of a plurality of liquid crystal molecules contained in each of the liquid crystal regions is concentric along the polymer walls within a plane which is in parallel with the substrates.

In another embodiment, each of the liquid crystal regions has a plurality of liquid crystal domains and an orientation direction of each of the liquid crystal domains is concentric along the polymer walls within a plane which is in parallel with the substrates.

45 In another embodiment, each of the liquid crystal regions has an inside liquid crystal domain situated in a center thereof, a polymer region surrounding an outside of the inside liquid crystal domain, and a plurality of outside liquid crystal domains surrounding an outside of the polymer region; and the respective outside liquid crystal domains are aligned in a radial manner within a plane which is in parallel with the substrates.

50 In another embodiment, the liquid crystal regions have a plurality of liquid crystal domains, and an orientation direction of each of the liquid crystal domains is different within a plane which is in parallel with the substrates.

In another embodiment, the liquid crystal regions have a polymer region positioned in the center thereof and a plurality of liquid crystal domains surrounding an outside of the polymer region, and the respective liquid crystal domains are aligned in a radial manner within a plane which is in parallel with the substrates.

55 In another embodiment, the liquid crystal display device of the present invention includes a plurality of pixels, and the liquid crystal regions are provided in at least one pixel.

In another embodiment, at least one liquid crystal region contained in the pixel has a size of 30% or more of the pixel size.

In another embodiment, an orientation direction of a plurality of liquid crystal molecules contained in each



of the liquid crystal regions is concentric along the polymer walls within a plane which is in parallel with the substrates.

5 In another embodiment, each of the liquid crystal regions has a plurality of liquid crystal domains, and an orientation direction of each of the liquid crystal domains is concentric along the polymer walls within a plane which is in parallel with the substrates.

10 In another embodiment, the liquid crystal regions have an inside liquid crystal domain positioned in a center thereof, a polymer region surrounding an outside of the inside liquid crystal domain, and a plurality of outside liquid crystal domains surrounding an outside of the polymer region; and the respective outside liquid crystal domains are aligned in a radial manner within a plane which is in parallel with the substrates.

In another embodiment, the liquid crystal regions have a plurality of liquid crystal domains, and an orientation direction of each of the liquid crystal domains is different within a plane which is in parallel with the substrates.

15 In another embodiment, the liquid crystal regions have a polymer region positioned in a center thereof and a plurality of liquid crystal domains surrounding an outside of the polymer region; and the respective liquid crystal domains are aligned in a radial manner within a plane which is in parallel with the substrates.

In another embodiment, a liquid crystal display device of the present invention includes a plurality of pixels, and two or more of the liquid crystal regions are entirely or partially provided in one pixel.

In another embodiment, the pixel has a longitudinal side of 200  $\mu\text{m}$  or more.

20 In another embodiment, an orientation direction of a plurality of liquid crystal molecules contained in the liquid crystal regions are concentric along the polymer walls within a plane which is in parallel with the substrates.

25 In another embodiment, each of the liquid crystal regions has a plurality of liquid crystal domains, and an orientation direction of each of the liquid crystal domains is concentric along the polymer walls within a plane which is in parallel with the substrates.

In another embodiment, each of the liquid crystal domains has an inside liquid crystal domain positioned in a center thereof, a polymer region surrounding an outside of the inside liquid crystal domain, and a plurality of liquid crystal domains surrounding an outside of the polymer region; and the respective outside liquid crystal domains are aligned in a radial manner within a plane which is in parallel with the substrates.

30 In another embodiment, the liquid crystal region has a plurality of liquid crystal domains, and an orientation direction of each of the liquid crystal domains is different within a plane which is in parallel with the substrates.

In another embodiment, each of the liquid crystal regions has a polymer region positioned in a center thereof and a plurality of liquid crystal domains surrounding an outside of the polymer region, and the respective liquid crystal domains are aligned in a radial manner within a plane which is in parallel with the substrates.

35 In another embodiment, a plurality of liquid crystal molecules contained in each of the liquid crystal regions are aligned in a helical manner along a helical axis which is vertical with respect to the substrates.

In another embodiment, the plurality of liquid crystal molecules contained in each of the liquid crystal regions are provided with a helical pitch of 15  $\mu\text{m}$  to 100  $\mu\text{m}$ .

40 In another embodiment,  $d \times \Delta n$  is in the range of 0.4  $\mu\text{m}$  to 1.1  $\mu\text{m}$ ; and a distance between the substrates is in the range of 3  $\mu\text{m}$  to 10  $\mu\text{m}$ , where  $d$  is a thickness between horizontal portions in each of the liquid crystal regions and  $\Delta n$  is anisotropy of refractive index thereof.

In another embodiment, the display medium has a structure in which a liquid crystalline compound is fixed in the vicinity of an interface between the liquid crystal region and the polymer wall.

45 In another embodiment, anisotropy of dielectric constant  $\Delta\epsilon_L$  of the liquid crystal region and anisotropy of dielectric constant  $\Delta\epsilon_P$  of the liquid crystalline compound have a relationship of  $\Delta\epsilon_L \times \Delta\epsilon_P < 0$ .

In another embodiment, the liquid crystalline compound has at least one of a fluorine atom and a chlorine atom and the liquid crystal region is formed from a liquid crystal material having at least one of fluorine atom and a chlorine atom in its molecule.

50 In another embodiment, the liquid crystalline compound has an optically active group in its molecule and the liquid crystal region is formed from ferroelectric liquid crystal.

In another embodiment, the polymer walls are formed in a liquid crystal state.

In another embodiment, the liquid crystal regions and the polymer walls contain a dichroic dye.

In another embodiment, the polymer walls are formed in a liquid crystal state, and the polymer walls and the liquid crystal regions are in the same orientation when no voltage is applied to the display medium.

55 In another embodiment, at least one of the substrates has an orientation film in contact with the display medium, and the polymer walls and the liquid crystal regions are in the same orientation, based on the orientation film.

In another embodiment, the liquid crystal regions and the polymer walls contain a dichroic dye.

In another embodiment, anisotropy of dielectric constant  $\Delta\epsilon_L$  of the liquid crystal region and anisotropy of

dielectric constant  $\Delta\epsilon_P$  of the liquid crystalline compound have a relationship of  $\Delta\epsilon_L \times \Delta\epsilon_P < 0$ .

In another embodiment, a remaining monomer ratio obtained from infrared absorption caused by a double bond between carbons in the polymer wall and infrared absorption caused by a carbonyl group of an ester in the polymer wall is 10% or less.

In another embodiment, a light-intercepting mask is placed on one of the substrates so that light-intercepting portions of the mask cover portions where the substrate and the polymer walls are in contact with each other.

In another embodiment, the light-intercepting mask is placed so that the light-intercepting portions thereof cover 50% or more of the respective portions where the substrate and the polymer walls are in contact with each other.

In another embodiment, orientation films are respectively formed on the electrodes mounted on the substrates.

In another embodiment, the orientation films are uniaxially aligned by an orientation treatment.

In another embodiment, at least one of the orientation films contain a photopolymerization initiator.

In another embodiment, a polarizing plate is provided outside of at least one of the substrates.

In another aspect of the present invention, a method for manufacturing a liquid crystal display device having a plurality of pixels, includes the steps of:

providing a mixture containing a photopolymerizable compound and a liquid crystal material between a pair of substrates, two substrates facing each other, at least one of the substrates being transparent, and electrodes being disposed on inside surfaces of the respective substrates, thereby forming a cell; and

irradiating the mixture with light under the condition that intensity of light is reduced in predetermined portions of the mixture, thereby forming a display medium between the substrates, the display medium having polymer walls containing a polymer as their main component and liquid crystal regions containing liquid crystal as their main component.

In one embodiment, the predetermined portions correspond to at least one pixel, whereby the liquid crystal regions are provided in at least one pixel.

In another embodiment, an area of each of the predetermined portions corresponds to 30% or more of each pixel area, whereby at least one liquid crystal region contained in the pixel is made 30% or more of the pixel area.

In another embodiment, intensity of light is reduced by using a photomask, and the photomask is placed on the side of the display medium of one of the substrates.

In another embodiment, the mixture is irradiated with light through a photomask, the photomask having a plurality of masking portions for forming the liquid crystal regions and each of the masking portion having at least one light transmission hole at least in a center thereof, whereby liquid crystal domains are formed in a radial manner in each of the liquid crystal regions.

In another embodiment, the method for manufacturing a liquid crystal display device of the present invention uses a photomask having masking portions for forming the liquid crystal regions, each of the masking portions having a light transmission hole in a center thereof and light transmission slits disposed in a radial manner around the transmission hole.

In another embodiment, the mixture is irradiated with light while alternating a light-irradiating period and a non light-irradiating period.

In another embodiment, the mixture further contains a compound having effects for suppressing photopolymerization.

In another embodiment, the display medium having walls containing a polymer as their main component and liquid crystal regions containing liquid crystal as their main component is formed between the substrates by irradiating light to all of the portions or part thereof excluding the pixels.

In another embodiment, light which is irradiated to all of the portions or part thereof excluding the pixels is linear light.

In another embodiment, light irradiation to all of the portions or part thereof excluding the pixels is conducted while spot light in a dot shape is moved.

In another embodiment, intensity of light is reduced by using an insulating film formed on the electrode of one of the substrates, and the display medium having walls containing a polymer as its main component and liquid crystal regions containing liquid crystal as its main component is formed between the substrates by irradiating light to the mixture from the side of the substrate on which the insulating film is formed.

In another embodiment, the step of forming a cell is conducted by attaching the two substrates after providing the mixture on one of the substrates.

In another embodiment, polarizing plates are formed on external surfaces of the two substrates.

In another aspect of the present invention, a method for manufacturing a liquid crystal display device hav-

ing a plurality of pixels, includes the steps of:

forming an orientation film containing a photopolymerization initiator on at least one of a pair of substrates, two substrates facing each other, at least one of the substrates being transparent, and electrodes being disposed on inside surfaces of the respective substrates;

subjecting the substrate on which the orientation film is formed to a rubbing treatment in one direction;

providing a mixture containing a photopolymerizable compound and a liquid crystal material between the pair of substrates after the rubbing treatment; and

forming a display medium having polymer walls containing a polymer as their main component and liquid crystal regions containing liquid crystal as their main component by curing the photopolymerizable compound.

In one embodiment, the photopolymerizable compound contained in the mixture contains a liquid crystalline compound having at least one polymerizable functional group in its molecule.

In another embodiment, a compound having a polymerizable functional group, at least one of a fluorine atom and a chlorine atom in its molecule is used as the liquid crystalline compound, and a liquid crystal material having at least one of a fluorine and a chlorine atom in its molecule is used for the liquid crystal regions.

In another embodiment, a compound having a polymerizable functional group and an optically active group in its molecule is used as the liquid crystalline compound, and ferroelectric liquid crystal is used for the liquid crystal regions.

In another embodiment, UV-rays are irradiated to the mixture so that portions where the liquid crystal regions are to be formed become weak light-irradiated regions, thereby optically polymerizing the photopolymerizable compound.

In another embodiment, weak light-irradiated regions are formed by using a photomask, and the photomask is placed on the side of the display medium of one of the substrates.

In another embodiment, the step of forming a cell is conducted by attaching the two substrates after providing the mixture on one of the substrates.

In another embodiment, polarizing plates are formed on external surfaces of the two substrates.

In another aspect of the present invention, a method for manufacturing a liquid crystal display device having a plurality of pixels, includes the steps of:

forming a thin film pattern containing a photopolymerization initiator on one surface of at least one of a pair of substrates, the substrates respectively having electrodes and at least one of the substrates being transparent;

providing a mixture containing a polymerizable compound and a liquid crystal material between the pair of substrates, at least one of the substrates having the thin film pattern, thereby forming a cell; and

forming a display medium between the substrates by curing the polymerizable compound, the display medium having polymer walls containing a polymer as their main component and liquid crystal regions containing liquid crystal as their main component.

In one embodiment, the polymerization initiator is a photopolymerization initiator, the polymerizable compound is a photopolymerizable compound, a photomask allowing 50% or more of the thin film pattern to be exposed is placed outside of one of the substrates, and light is irradiated to the photopolymerizable initiator and the photopolymerizable compound through the photomask to cure the photopolymerizable compound.

In another embodiment, the photopolymerizable compound contained in the mixture contains a liquid crystalline compound having at least one kind of polymerizable functional group at its molecule.

In another embodiment, a compound having a polymerizable functional group, and at least one of a fluorine atom and a chlorine atom in its molecule is used as the liquid crystalline compound; and a liquid crystal material having at least one of a fluorine atom and a chlorine atom in its molecule is used for the liquid crystal regions.

In another embodiment, a compound having a polymerizable functional group and an optically active group in its molecule is used as the liquid crystalline compound and ferroelectric liquid crystal is used for the liquid crystal regions.

In another embodiment, UV-rays are irradiated to the mixture so that portions where the liquid crystal regions are to be formed become weak light-irradiated regions, thereby optically polymerizing the polymerizable compound.

In another embodiment, the polymerization initiator is a heat polymerization initiator, the polymerizable compound is a heat polymerizable compound, and the heat polymerization initiator and the mixture are heated to cure the heat polymerizable compound.

In another embodiment, the step of forming a cell is conducted by attaching the two substrates after providing the mixture on one of the substrates.

In another embodiment, polarizing plates are formed on external surfaces of the two substrates.

In another aspect of the present invention, a method for manufacturing a liquid crystal display device having a plurality of pixels, includes the steps of:

providing a mixture between a pair of substrates facing each other, thereby forming a cell, at least one of the substrates being transparent, electrodes being disposed on inside surfaces on the respective substrates, the mixture containing a liquid crystal material, a polymerizable liquid crystalline material having a liquid crystalline functional group in its molecule, a polymerizable compound, and a polymerization initiator, anisotropy of dielectric constant  $\Delta\epsilon_L$  of the liquid crystal material and anisotropy of dielectric constant  $\Delta\epsilon_P$  of the polymerizable liquid crystalline material having a relationship of  $\Delta\epsilon_L \times \Delta\epsilon_P < 0$ , and

forming a display medium between the substrates by polymerizing the polymerizable compound, the display medium having polymer walls containing a polymer as their main component and liquid crystal regions containing liquid crystal as their main component, providing the liquid crystalline functional groups in the liquid crystal regions to fix a liquid crystalline polymer on the polymer walls.

In one embodiment, the polymerizable compound is a photopolymerizable compound, the polymerization initiator is a photopolymerization initiator, and the polymerizable compound is optically polymerized.

In another embodiment, UV-rays are irradiated to the mixture so that portions where the liquid crystal regions are to be formed become weak light-irradiated regions, thereby optically polymerizing the mixture.

In another embodiment, the weak light-irradiated regions are formed by using a photomask, and the photomask is placed on the side of the display medium of one of the substrates.

In another embodiment, the polymerizable compound is a heat polymerizable compound, the polymerization initiator is a heat polymerization initiator, and the polymerizable compound is polymerized by heating.

In another embodiment, a compound having at least one of a fluorine atom and a chlorine atom in its molecule is used as the liquid crystal material and the polymerizable liquid crystalline material.

In another embodiment, the step of forming a cell is conducted by attaching the two substrates after providing the mixture on one of the substrates.

In another embodiment, the step of forming a cell includes the steps of:

coating the mixture onto one of the substrates, the mixture further containing a solvent capable of homogeneously dissolving the liquid crystal material and the polymerizable liquid crystalline material;

removing the solvent from the mixture coated onto one of the substrates by evaporation to provide the liquid crystalline functional groups in the liquid crystal regions, thereby fixing a liquid crystalline compound on the polymer walls; and

placing the other substrate on the substrate on which the mixture is coated.

In another embodiment, polarizing plates are formed on external surfaces of the two substrates.

In another aspect of the present invention, a method for manufacturing a liquid crystal display device having a plurality of pixels, includes the steps of:

providing a mixture between a pair of substrates facing each other, thereby forming a cell, at least one of the substrates being transparent, electrodes being disposed on inside surfaces of the respective substrates, the mixture containing a liquid crystal material, a photopolymerizable compound, photopolymerization initiator, and a radical generating agent;

irradiating light to the mixture to cause a phase separation, thereby obtaining a state in which liquid crystal regions are dispersed in the polymer walls; and

thermally decomposing the radical generating agent by heating the display medium.

In another embodiment, UV-rays are irradiated to the mixture so that portions where the liquid crystal regions are to be formed become weak light-irradiated regions, thereby optically polymerizing the polymerizable compound.

In another embodiment, the weak light-irradiated regions are formed by a photomask, and the photomask is placed on the side of the display medium of one of the substrates.

In another embodiment, a liquid crystal material of at least one of a fluorine type and chlorine type is used as the liquid crystal material.

In another embodiment, the photopolymerizable compound contains a photopolymerizable liquid crystal compound.

In another embodiment, the step of forming a cell is conducted by attaching the two substrates after providing the mixture on one of the substrates.

In another embodiment, polarizing plates are formed on external surfaces of the two substrates.

Thus, the invention described herein makes possible the advantages of (1) providing a light scattering type liquid crystal display device in which liquid crystal regions in a drop shape, each having the same diameter, are formed with regularity in a direction along a surface of a substrate and which has a steep threshold characteristic curve and excellent contrast, and a method for manufacturing the same; (2) providing a non light scattering type liquid crystal display device in which liquid crystal regions are formed under the condition that the size of liquid crystal regions is adjusted with respect to pixels, and a method for manufacturing the same; (3) providing a liquid crystal display device in which the response speed is sufficiently improved and a high elec-

trical holding ratio is maintained, and a method for producing the same; (4) providing a liquid crystal display device in which unreacted substances such as an unreacted monomer remaining in a display medium is reduced so as not to cause peeling between the substrate and the display medium, and a method for manufacturing the same; (5) providing a liquid crystal display device in which each liquid crystal region can be provided with respect to pixels without a photomask by causing a phase separation between the liquid crystal and the polymer without allowing the liquid crystal and the polymer to be mixed with each other; and (6) providing a liquid crystal display device which can greatly contribute to the improvement of shock resistance of the liquid crystal display device using ferroelectric liquid crystal, and a method for manufacturing the same.

These and other advantages of the present invention will become apparent to those skilled in the art upon reading and understanding the following detailed description with reference to the accompanying figures.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a cross-sectional view showing a liquid crystal display device of Example 1.

Figure 2A is a cross-sectional view showing the state of the liquid crystal display device of Example 1 before being irradiated with light.

Figure 2B is a cross-sectional view showing the state of the liquid crystal display device of Example 1 after being irradiated with light.

Figure 3 is a view showing boundary regions between polymer walls cured by being irradiated with light and liquid crystal according to Example 1.

Figure 4 is a plan view of a photomask used in the case where one liquid crystal region is provided for one pixel electrode.

Figure 5A is a plan view of a photomask used in the case where one liquid crystal region is provided for two pixel electrodes.

Figure 5B is a plan view of a photomask used in the case where one liquid crystal region is provided for one row of pixel electrodes.

Figure 6 is a cross-sectional view of a liquid crystal display device in which liquid crystal regions are made larger than those of Figure 2B, whereby the liquid crystal regions are formed closer to the pixel electrodes.

Figure 7 is a plan view of a cell, illustrating a method for injecting a mixture into the cell by vacuum injection.

Figure 8 is a cross-sectional side view of the cell shown in Figure 7.

Figure 9 is a front view showing an injector.

Figure 10A is a cross-sectional view showing a liquid crystal display device with an orientation film applicable to the present invention, where the size of liquid crystal regions is slightly smaller than that of pixel electrodes.

Figure 10B is a cross-sectional view showing a liquid crystal display device with an orientation film applicable to the present invention, where the size of liquid crystal regions is larger than that of the pixels.

Figure 11A is a view showing an orientation state of liquid crystal molecules in a conventional ECB liquid crystal display device under no applied voltage.

Figure 11B is a view showing an orientation state of liquid crystal molecules in a conventional ECB liquid crystal display device under an applied voltage.

Figure 12A is a view showing an orientation state of liquid crystal molecules in an ECB liquid crystal display device according to the present invention under no applied voltage.

Figure 12B is a view showing an orientation state of liquid crystal molecules in the ECB liquid crystal display device according to the present invention under an applied voltage.

Figure 13 is a view showing boundary regions between polymer walls and liquid crystal in a liquid crystal display device of Comparative Example 6.

Figure 14 is a plan view showing another photomask used in the present invention.

Figure 15 is a plan view showing another photomask used in the present invention.

Figure 16 is a plan view showing still another photomask used in the present invention.

Figure 17 is a view showing the case where a plurality of liquid crystal regions are formed in one pixel according to the present invention.

Figure 18 shows a structure in which the viewing angle dependency is further improved in the liquid crystal display device according to the present invention.

Figure 19 is a cross-sectional view showing still another example of a liquid crystal display device of the present invention.

Figure 20 is a plan view showing a photomask used for manufacturing the liquid crystal display device shown in Figure 19.

Figure 21 is a plan view showing a light-intercepting mask provided in the liquid crystal display device

shown in Figure 19.

Figure 22 is a view showing a liquid crystal region of a light scattering type.

Figure 23 is a view showing a liquid crystal region of a non light scattering type obtained in the case where the photopolymerization speed is high.

Figure 24A is a view showing a liquid crystal region of a non light scattering type obtained in the case where the photopolymerization speed is low.

Figure 24B is a view showing another liquid crystal regions of a non light scattering type obtained in the case where the photopolymerization speed is low.

Figure 24C is a view showing another liquid crystal region of a non light scattering type obtained in the case where the photopolymerization speed is low.

Figure 24D is a view showing another liquid crystal region of a non light scattering type obtained in the case where the photopolymerization speed is low.

Figure 25 is a view showing a liquid crystal region of a non light scattering type obtained in the case where the photopolymerization speed is higher than that of Figures 24A to 24D and lower than that of Figure 23.

Figure 26A is a view showing a liquid crystal region of a non light scattering type obtained in the case where the photopolymerization speed is still lower.

Figure 26B is a view showing another liquid crystal region of a non light scattering type obtained in the case where the photopolymerization speed is still lower.

Figure 26C is a view showing another liquid crystal region of a non light scattering type obtained in the case where the photopolymerization speed is still lower.

Figure 26D is a view showing another liquid crystal region of a non light scattering type obtained in the case where the photopolymerization speed is still lower.

Figure 27 is a view showing a liquid crystal region of a non light scattering type obtained in the case where a light transmission hole is provided in the center of a masking portion of a photomask.

Figure 28A is a front cross-sectional view of a liquid crystal region of a liquid crystal display device of Example 4, where the helical pitch is in the range of 15  $\mu\text{m}$  to 100  $\mu\text{m}$ .

Figure 28B is a plan view showing the liquid crystal region shown in Figure 28A.

Figure 28C is a plan view for each of the layers I, II, III, and IV of the liquid crystal region shown in Figure 28A.

Figure 29A is a front cross-sectional view of a liquid crystal region of a liquid crystal display device of Example 4, where the helical pitch is more than 100  $\mu\text{m}$ .

Figure 29B is a plan view showing the liquid crystal region shown in Figure 29A.

Figure 29C is a plan view for each of the layers I, II, III, IV layers of the liquid crystal region shown in Figure 29A.

Figure 30A is a front cross-sectional view of a liquid crystal region of a liquid crystal display device of Example 4, where the helical pitch is smaller than 15  $\mu\text{m}$ .

Figure 30B is a plan view showing the liquid crystal region shown in Figure 30A.

Figure 31 is a plan view showing an example of a photomask used in Example 5.

Figure 32 is a plan view showing an example of a photomask used in Example 6.

Figure 33 is a plan view showing liquid crystal regions obtained by using the photomask shown in Figure 32.

Figure 34A is a graph showing the viewing angle characteristic in the a direction of a liquid crystal display device of Example 6.

Figure 34B is a graph showing the viewing angle characteristic in the b direction of a liquid crystal display device of Example 6.

Figure 34C is a graph showing the viewing angle characteristic in the c direction of a liquid crystal display device of Example 6.

Figure 34D is a view showing the relationship between the a, b, and c directions.

Figure 35 is a cross-sectional view showing a polymer dispersed liquid crystal display device of Example 9.

Figure 36 is a cross-sectional view showing one step of a method for manufacturing the liquid crystal display device shown in Figure 35.

Figure 37 is a cross-sectional view showing a polymer dispersed liquid crystal display device of Example 10.

Figure 38 is a cross-sectional view showing one step of a method for manufacturing a liquid crystal display device shown in Figure 37.

Figure 39 is a schematic view showing an example of a shape for the thin film pattern of Example 10.

Figure 40 is a schematic view showing another example of a shape for the thin film pattern of Example 10.

10.

Figure 41 is a schematic view showing another example of a shape for the thin film pattern of Example

10.

Figure 42 is a cross sectional view showing a liquid crystal display device of Example 11.

Figure 43 is a plan view showing a map for crossing electrode lines in the liquid crystal display device of Example 11.

Figure 44A is a view showing a state in which a conventional ECB liquid crystal display device performs a half tone display in a half tone.

Figure 44B is a view showing a state in which the ECB liquid crystal display device of Example 11 performs a 1/2 tone display.

Figure 45A is a view showing the orientation state of liquid crystal molecules in the GH liquid crystal display device of Example 11 under no applied voltage.

Figure 45B is a view showing the orientation state of liquid crystal molecules in the GH liquid crystal display device of Example 11 under an applied voltage.

Figure 46 is a cross-sectional view showing a liquid crystal display device of a light scattering type applicable to the present invention

Figure 47 is a cross-sectional view showing one step of a method for manufacturing a polymer dispersed liquid crystal display device of Application 39.

Figure 48 is a perspective view of Figure 47.

Figure 49 is a cross-sectional view showing one step of a method for manufacturing a surface stabilized ferroelectric liquid crystal (SSFLC) display device of Application 40.

Figure 50 is a perspective view of Figure 49.

Figure 51 is a cross-sectional view showing one step of a method for manufacturing a surface stabilized ferroelectric liquid crystal (SSFLC) display device of Application 41.

## **DESCRIPTION OF THE PREFERRED EMBODIMENTS**

According to the present invention, a mixture containing, at least, a light-curable material and a liquid crystal material is inserted between two substrates, each substrate having electrodes. The inserted mixture is then irradiated with light under the condition that the intensity of light is reduced in places where liquid crystal regions of the mixture are to be formed.

The light-curable material which is present in regions to which light is irradiated, reacts to form a core for a polymer wall. After that, a concentration gradient of the material is formed due to the decrease in the concentration of the material in the light-irradiated regions. Along this concentration gradient, an unreacted material in regions, to which light having low intensity is irradiated masking portions (the masking portions do not intercept light completely, but weaken the intensity of light) of a photomask, gathers in the light-irradiated regions and is polymerized to form polymer walls. In regions where the polymer walls are not formed, liquid crystal regions are formed.

In this case, the position of the weak light-irradiated regions is set in accordance with the position of the liquid crystal regions to be formed in the display medium. When the mixture is irradiated with light, liquid crystal regions are formed in the weak light-irradiated regions. At this time, if light is irradiated to the mixture by using a photomask having relatively small masking portions, nearly spherical liquid crystal regions are formed in the weak light-irradiated regions. Thus, the resulting liquid crystal display device becomes a light scattering type. Figure 22 shows liquid crystal regions of a light scattering type. A number of liquid crystal regions *d* are formed in one pixel *b* and the diameter of each liquid crystal region *d* is very small.

A light scattering type refers to a system in which light scattering and transparent states of a liquid crystal display device in which liquid crystal molecules are dispersed in a polymer are electrically regulated. A principle thereof is that the refractive index of liquid crystal molecules is set so as to almost coincide with that of a polymer during the application of a voltage. In this case, while a voltage is applied, the liquid crystal display device is in a transparent state. In contrast, when no voltage is applied, the liquid crystal molecules are in a random orientation due to interaction with the polymer walls, whereby the apparent refractive index of the liquid crystal molecules is increased to cause mismatching with the refractive index of the polymer walls. Thus, the liquid crystal molecules take a light scattering state.

The mixture of light-curable material and liquid crystal material is inserted between two substrates, each having electrodes with at least one of the substrates being transparent. The mixture is irradiated with light under the condition that the intensity of light is reduced in portions of the mixture which correspond to at least 30% of the size of each pixel. As a means for reducing the intensity of light, a photomask or the like is used. The mixture is irradiated with light through the photomask or the like.

In portions of the mixture to which light with higher intensity is irradiated, the polymer material is cured to form walls reaching the inside surfaces of both substrates. Liquid crystal regions are formed in portions partitioned by the walls. That is, the liquid crystal regions are formed in a dispersed state.

When the mixture is irradiated with light by using a photomask or the like having relatively large masking portions, liquid crystal regions are widened and have portions which are in parallel with the surface of the substrates. The parallel portions are formed in the vicinity of both substrates. The resulting liquid crystal display device is a non light scattering type. A non light scattering type refers to a system in which light scattering caused by the above-mentioned difference in refractive index between the liquid crystal region and the polymer wall is reduced as much as possible and a display is performed only by the change of the orientation of liquid crystal molecules. Examples of a method for taking advantage of the change of the orientation of liquid crystal molecules include a mode in which the change of the refractive index is taken by using polarizing plates (e.g., a TN mode and an ECB mode); and a guest-host (GH) mode in which a dichroic dye is added to liquid crystal without using a polarizing plate.

In the non light scattering type liquid crystal display device, each liquid crystal region can be provided in one pixel, each liquid crystal region can be provided in two or more pixels, or a plurality of liquid crystal regions can be provided in one pixel by appropriately regulating means for reducing the intensity of light such as a photomask. In addition, even though the size of a pixel may be large, one or more liquid crystal region(s) can entirely be provided in one pixel; some parts of the liquid crystal regions are provided in one pixel; or one or more entire liquid crystal regions and some parts thereof are provided in one pixel.

Moreover, it is also possible that a homogeneous mixture of a light-curable material and a liquid crystal material is dropped or coated onto one substrate, then two substrates are attached to each other, and the light-curable material is cured.

In particular, in the case where a photomask is used, portions to which light is irradiated are clearly limited. Thus, even in the case where a plurality of liquid crystal regions are formed in one pixel, the polymer can be provided in a large amount outside the pixel, so that contrast can be improved, which is preferred.

In the production of the non light scattering type liquid crystal display device, the photopolymerization rate is changed by varying materials of the mixture and conditions of light irradiation, whereby a phase separation rate of a polymer and liquid crystal can be regulated.

(1) The case where the phase separation rate (i.e., photopolymerization rate) is high:

Due to light leaked from the light-irradiated regions, photopolymerization of a polymerizable material is also conducted in the weak light-irradiated regions, and thus, a plurality of liquid crystal regions are formed therein. In this case, as shown in Figure 23, each liquid crystal region **d** present in a pixel **b** is in the form of a circle, when seen from the upper side of the substrate, the orientation direction of the liquid crystal molecules in the crystal regions **d** is in the form of concentric circles along the polymer walls and is nearly in parallel with the surface of the substrate. When an electrical field is applied to this display medium so that a half tone is obtained, the liquid crystal molecules stand omnidirectionally, so that the apparent refractive index becomes almost the same, even when seen from any directions, and viewing angle characteristics are improved, resulting in satisfactory contrast.

(2) The case where the phase separation rate, (i.e., photopolymerization rate) is low:

A photopolymerization reaction is decreased in the weak light-irradiated regions and the shape of each liquid crystal region becomes almost the shape of the masking portions of a photomask. However, light-curable materials present in the weak light-irradiated regions cannot completely reach the portions where the polymerization of the polymerizable material (i.e., light-irradiated regions) is conducted. As shown in Figure 24A, 24B, 24C, or 24D, an inside liquid crystal region **d** is formed almost in the center of each pixel **b** (the weak light-irradiated region, in this case), and a polymer region **f** and an outside liquid crystal region **d'** are formed so as to surround the inside liquid crystal region **d**. Thus, the outside liquid crystal region **d'** is formed, for example, in a donut shape or in a C shape.

Liquid crystal in the inside liquid crystal region **d** formed almost in the center of the pixel **b** has the same orientation as that described in the above-mentioned case (1). The liquid crystal region in a donut shape or the C-shaped liquid crystal region contains a plurality of liquid crystal domains **g**, and the plurality of liquid crystal domains **g** are formed almost in a radial manner with respect to the center of each pixel. Here, the respective liquid crystal domains **g** have different orientations from each other even though a polymer in a wall shape is not present between the liquid crystal domains **g**, and discrimination lines (actually, interfaces) are present between the liquid crystal domains **g**.

This phenomenon is caused as follows:

Since a polymerization reaction is conducted while light-curable polymers move, the liquid crystal molecules are oriented in a vertical direction with respect to the polymer walls. Moreover, in the case where the liquid crystal regions become large, the same phenomenon can be seen.



When an electrical field is applied to a display medium which has the above-mentioned orientation state, the inside liquid crystal region **d** almost in the center of the pixel **b** has the same orientation as that of the above-mentioned case (1). In contrast, in the outside liquid crystal region **d'** in a donut shape or in a C shape, the direction in which the liquid crystal molecules stand is different in each domain, so that the characteristics of the angle of visibility, i.e., viewing angle characteristics are remarkably improved in the same principle as that described in the above-mentioned case (1). If a photopolymerization rate is slightly higher than this case, liquid crystal regions as shown in Figure 25 are obtained. As is understood in Figure 25, a plurality of circular liquid crystal regions **d2** are formed so as to be in contact with each other on the edges of pixel **b** and a plurality of circular liquid crystal regions **d1** are formed so as to be surrounded by the liquid crystal regions **d2**.

(3) The case where the phase separation rate (i.e., photopolymerization rate) is further lowered:

The polymers remaining in the weak light-irradiated regions are further decreased, and the liquid crystal regions which have almost the same shape as that of the masking portions of a photomask are formed. In this case, as shown in Figure 26A, 26B, 26C, or 26D, each liquid crystal region **d** contains a plurality of liquid crystal domains **g** and the discrimination lines **h** between the liquid crystal domains **g** become vertical with respect to the polymer walls. The orientation of the liquid crystal molecules in the liquid crystal region **d** become random since an island portion is not present in the center of the liquid crystal region **d**. At this time, if a hole for allowing light to pass through is provided in the center of the masking region (corresponding to the pixel **b**) of a photomask, an island **i** made of a polymer can be formed in the center of the liquid crystal region **d** as shown in Figure 27, whereby the liquid crystal domains **g** are formed in a radial manner with respect to the island **i**.

When an electrical field is applied to this display medium, the liquid crystal molecules move in the same way as in the above-mentioned case (2). The refractive index of the liquid crystal molecules is almost the same when seen from an omnidirection with a predetermined angle from a vertical direction to the substrate surface. Thus, the viewing angle characteristics can be improved. This case is preferred since the ratio of the liquid crystal regions with respect to pixel(s) is increased and contrast is improved.

In the above-mentioned cases (2) and (3), if a chiral agent is added to the mixture, a plurality of liquid crystal molecules contained in a liquid crystal region are as shown in Figures 28A, 28B, and 28C. That is, when the liquid crystal region **d** is seen through the substrate, a plurality of domains **g** are formed in a radial manner as shown in Figure 28B; however, as shown in Figure 28A, the respective liquid crystal molecules **j** are aligned in a helical manner around the helical axis **k** which is almost vertical with respect to the surface of the substrate. More specifically, when the I layer of Figure 28A is seen through the substrate, the I layer is disposed as shown in Figure 28C. When the II, III, and IV layers of Figure 28A are seen through the substrate, the II, III, and IV layers are disposed as shown in Figure 28C.

On the other hand, when a chiral agent is not added to the mixture, a plurality of liquid crystal molecules are aligned as shown in Figures 29A, 29B, and 29C. When the liquid crystal region **d** is seen through the substrate, a plurality of domains **g** are disposed in a radial manner as shown in Figure 29B; however, as shown in Figure 29A, the respective liquid crystal molecules are aligned in a predetermined direction around the axis **1** which is almost vertical with respect to the surface of the substrate. More specifically, when the I layer of Figure 29A is seen through the substrate, the I layer is disposed as shown in Figure 29C, and when the II, III, and IV layers of Figure 29A are seen through the substrate, the II, III, and IV layers are disposed as shown in Figure 29C.

When an excess amount of a chiral agent is added to the mixture, as shown in Figure 30B, when the liquid crystal region **d** is seen through the substrate, a plurality of domains **g** are disposed in a radial manner; however, as shown in Figure 30A, the helical axis becomes parallel with the surface of the substrate even though the liquid crystal molecules are aligned in a helical manner. This phenomenon is caused even in the case where cholesteric liquid crystal is added to nematic liquid crystal, in addition to the case where a chiral agent is added to the mixture.

Furthermore, the liquid crystal regions are formed in each pixel, and a light-intercepting mask is provided on one side of a liquid crystal layer (containing the liquid crystal regions and the polymer walls). At least 50% or more of the area of each polymer wall is covered with the light-intercepting mask, whereby light which is scattered at an interface between the polymer wall and the liquid crystal region can be prevented from being leaked outside. In particular, in the case where the light-intercepting mask is provided closer to the light incident side than the liquid crystal region, the incident light can be prevented from being scattered at an interface between the liquid crystal region and the polymer wall.

In a method for manufacturing a liquid crystal display device according to the present invention, an orientation film is formed on at least one of the substrates for the purpose of improving the regularity of the orientation of liquid crystal regions. The orientation film contains a photopolymerization initiator. Moreover, the sub-

strate on which the orientation film is formed is subjected to a rubbing treatment. When a cell is irradiated with light by using a photomask, a photopolymerizable compound material starts being cured due to the photopolymerization initiator contained in the orientation film. In this case, the curing speed of the photopolymerizable compound material is higher in regions to which strong light is irradiated than in regions to which weak light is irradiated. Moreover, in the regions to which strong light is irradiated, the phase separation speed between the liquid crystal and the cured polymer is higher. Thus, in the strong light-irradiated regions, the polymer is more rapidly deposited to push the liquid crystal into the weak light-irradiated regions. As a result, in the strong light-irradiated regions, polymer walls are formed, and in the weak light-irradiated regions, liquid crystal regions are formed, being in contact with the orientation film to be subjected to an orientation treatment. In this way, the liquid crystal regions are disposed with regularity in a planar manner.

There is another method for improving the regularity of the orientation of the liquid crystal regions. That is, a thin film pattern containing a photopolymerization initiator is formed on portions, where polymer walls are to be formed, of at least one of the substrates. After that, the polymerizable compound material in the mixture is cured by the irradiation of UV-rays or by heating. When the mixture is irradiated with UV-rays or heated, the polymerizable compound material starts being cured due to the polymerization initiator contained in the thin film pattern, whereby the polymer walls start being formed in contact with the thin film pattern. Because of this, the polymer walls are formed on the portions where the thin film pattern is formed, and the liquid crystal regions subjected to an orientation treatment are formed in one or a plurality of adjacent pixels.

In another example of the present invention, the liquid crystal material and a polymerizable compound material containing a liquid crystalline compound having at least one kind of polymerizable functional group in its molecule are polymerized. Due to this polymerization, a phase separation is caused, whereby a display medium in which the liquid crystal regions are partitioned by the polymer walls can be formed. Each liquid crystal region has a structure in which the liquid crystalline compound is fixed in the vicinity of the interface between the polymer wall and the liquid crystal region. Under this condition, the interfaces between the liquid crystal regions and the polymer walls are driven under an applied voltage; and the driving force is increased under no applied voltage since the liquid crystal molecules are bonded to the polymer walls. Thus, the response speed  $\tau_r$  under an applied voltage and a response speed  $\tau_d$  under no applied voltage can be improved. Moreover, since the liquid crystalline compound is fixed on the interfaces between the polymer walls and the liquid crystal regions, a phase separation is clearly conducted.

In the case where a liquid crystal material of a fluorine type and/or a chlorine type which is chemically stable is used as the liquid crystal material, the liquid crystal molecules will have chemical stability by using a polymerizable liquid crystalline compound having fluorine atom(s) and/or chlorine atom(s) in its molecule.

Moreover, in the case where ferroelectric liquid crystal is used as the liquid crystal material, it is possible to allow liquid crystal molecules having an optically active functional group to be present on the interfaces between the polymer walls and the liquid crystal regions by using a liquid crystalline compound having a polymerizable functional group and an optically active group in its molecule. Due to the presence of the liquid crystal molecules, the liquid crystal regions are influenced by the orientation regulating ability of the polymer walls having a component with a direction orthogonal with respect to the surface of the substrate as well as the orientation regulating ability of the substrate subjected to orientation treatment.

Furthermore, in the case where the polymer is cured in a liquid crystal state, the polymer as well as the liquid crystal regions are aligned in an orientation direction of the substrate. Thus, the orientation of the cell can be determined artificially by taking advantage of the orientation regulating ability of the substrate. In the case where a dichroic dye is contained in the liquid crystal regions and the polymer walls, when the liquid crystal regions and the polymer walls are aligned in the same direction, both of the liquid crystal regions and the polymer walls can be used as light transmission regions.

In another method for manufacturing a liquid crystal display device of the present invention, a liquid crystal material, a photopolymerizable liquid crystalline material having a liquid crystalline functional group in its molecules, a photopolymerizable compound material, and a photopolymerization initiator are polymerized; or a liquid crystal material, a heat polymerizable liquid crystalline material having a liquid crystalline functional group in its molecule, a heat polymerizable compound material, and a heat polymerization initiator are polymerized. Due to this polymerization, the polymerizable liquid crystalline material becomes a liquid crystalline polymer, and the liquid crystalline functional groups of the liquid crystalline polymer are provided in the liquid crystal regions, whereby a phase separation between the polymer and the liquid crystal is clearly conducted. When a voltage is applied from outside to the liquid crystal display device thus obtained, the liquid crystalline polymer can easily be moved in response to the application of a voltage. Namely, when a voltage is applied, the liquid crystal regions and the polymer walls are driven; and when no voltage is applied, the orientation of the liquid crystal molecules between the polymer walls and the liquid crystal regions is disturbed, whereby the molecules can rapidly move.

It is also possible that a mixture containing a liquid crystal material, a polymerizable liquid crystalline polymer having a liquid crystalline functional group in its molecule, and a solvent capable of homogeneously dissolving the liquid crystal material and the liquid crystalline polymer is coated onto one of the substrates and then the solvent is removed by evaporation. In this case, the liquid crystalline functional groups in the liquid crystalline polymer are provided in the liquid crystal regions in the same way as the above, whereby a phase separation between the polymer and the liquid crystal is clearly conducted.

In another method for manufacturing a liquid crystal display device of the present invention, a mixture inserted between facing substrates is irradiated with light, the mixture containing a liquid crystal material, a photosetting material, a photopolymerization initiator, and radical generating agent. Due to the light irradiation, a display medium in which the liquid crystal regions are dispersed in the polymer walls can be obtained. After that, the display medium is heated to thermally decompose the radical generating agent. As a result, a radical is generated from the radical generating agent, and the remaining monomer before heating is polymerized with the radical, decreasing the remaining monomer.

In still another method for manufacturing a liquid crystal display device of the present invention, all of the portions or part thereof excluding the pixels are irradiated with linear light to cure the photopolymerizable compound material contained in the mixture injected between the substrates. Due to this, a phase separation is easily conducted between the polymer and the liquid crystal under the condition that the polymer and the liquid crystal are not mixed with each other, the polymer walls are formed with regularity, and each liquid crystal region is regularly disposed in one or a plurality of pixels. According to the present invention, as other methods for curing the photopolymerizable compound material, the following two methods are used:

(1) Light in a spot shape is irradiated to all of the portions or part thereof excluding the pixels while the spot-shaped light is moved.

(2) An insulating film is formed on linear electrodes formed on one transparent substrate and light is irradiated to the substrate from the side thereof on which the insulating film is formed, whereby the polymerizable compound material of the mixture in the non-pixel portions which are not covered with the insulating film is cured.

In any of these methods, a phase separation between the polymer and the liquid crystal is easily conducted.

### Examples

Hereinafter, the present invention will be described by way of illustrating examples with reference to the drawings.

#### Example 1

The present invention will be described in the case where it is applied to a light scattering type liquid crystal display device.

Figure 1 is a cross-sectional view showing a liquid crystal display device of the present example. In the present example, two substrates 12 and 13 are provided so as to face each other with spacers (not shown) sandwiched therebetween. The substrate 12 is made of glass, and electrodes 11 made of ITO (indium tin oxide) are formed thereon. The substrate 13 is also made of glass; and a photomask 14 is provided on one surface of the substrate 13 and a counter electrode 15 made of ITO is formed on the other surface thereof.

A mixture containing a liquid crystal material and a light-curable material is sealed between the substrates 12 and 13. This mixture is irradiated with UV-rays 20 to cure the light-curable material. Consequently, a polymer dispersed liquid crystal layer in which liquid crystal regions 16 are partitioned by polymer walls 17 is obtained between the substrates 12 and 13.

The polymer dispersed liquid crystal display device thus obtained is observed as follows:

The polymer dispersed liquid crystal display device thus produced is cut and one substrate is peeled off from the other substrate in liquid nitrogen. The liquid crystal material is washed away with acetone, and a horizontal section of the polymer walls 17 is observed by a scanning electron microscope (SEM), revealing that the liquid crystal regions 16 which have the same regularity as that of a dot pattern of the photomask 14 and have a nearly uniform spherical shape with almost the same size are formed.

The present example has one characteristic: each interval  $a$  between the center of one liquid crystal region and the center of the adjacent liquid crystal region along the direction of a surface of the substrate is within a width of one pixel along this direction; and 80% or more of the intervals  $a$  satisfy a relationship:  $3b/2 > a > b/2$ , where  $b$  is an average of the intervals  $a$ .

The structure of each component applied to the present example and modified examples thereof will be

described below.

(A light regulating means such as a photomask)

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The study of the inventors of the present invention revealed the following:

Among portions of a photomask for forming light-irradiated regions and weak light-irradiated regions, in the case where the masking portions for forming the weak light-irradiated regions have a period of less than 2  $\mu\text{m}$ , the liquid crystal regions also have a diameter of less than 2  $\mu\text{m}$ . As a result, a number of liquid crystal regions on which visible light is not likely to be reflected are formed and light scattering under no voltage is decreased. In addition, the thickness between the substrates also influences the light scattering. That is, when the diameter of the masking portions of the photomask is smaller than the thickness between the substrates, liquid crystal regions to be formed have a honeycomb structure in the form of a circle, which causes the decrease in light scattering. Moreover, in this structure, when a voltage is applied, the liquid crystal display device cannot be in a sufficiently transparent state.

In the case where the period of the masking portions is more than 50  $\mu\text{m}$ , the diameter of liquid crystal regions to be formed has a period of more than 50  $\mu\text{m}$ . The liquid crystal regions occupy most of the part between the substrates, so that among light scattering characteristics, the masking characteristic is decreased. Thus, this structure is not preferred.

Accordingly, in view of the above-mentioned results, in the present example, the average range of a period of the masking portions is preferably in the range of 2  $\mu\text{m}$  to 50  $\mu\text{m}$ ; and more preferably in the range of 3  $\mu\text{m}$  to 20  $\mu\text{m}$ . When the period is taken as 20  $\mu\text{m}$  or less, intensity of light scattering can be increased as the size of a light scattering source (in this case, the liquid crystal regions) becomes closer to a wavelength of light, whereby a masking characteristic among the light scattering characteristics can be improved.

Under the above-mentioned limitations, the interval  $a$  between the center of one liquid crystal region and the center of the adjacent liquid crystal region along the direction of the surface of the substrate is within a width of one pixel along this direction; and 80% or more of the intervals  $a$  along this direction satisfies the relationship:  $3b/2 > a / b/2$ , where  $b$  is an average of the intervals  $a$ . More specifically, the regularity of the liquid crystal regions is increased.

Any shape of masking portions can be used as long as the intensity of UV-rays is controlled. In the present example, a masking portion corresponding to a circle, a square, a trapezoid, a hexagon, a rectangle, a diamond shape, a letter shape, a shape surrounded by a curved line(s) and/or a straight line(s) can be used, although it is not limited to these shapes. A configuration obtained by cutting a part of these shapes; a configuration obtained by the combination of the different shapes; a configuration obtained by the combination of the same shapes; and the like can be used. In the case where the configuration obtained by the combination of the same shapes is used, the average diameter of each masking portion is taken as a distance from a center of the configuration to an outermost portion thereof. In addition, when the present invention is put into practical use, one or more of these shapes are selected. In order to improve uniformity of the liquid crystal regions, it is preferred to limit the configuration to one shape with the same size.

Another characteristic of the present example is in that the liquid crystal regions are regularly aligned in a horizontal direction along the surface of the substrate. In this case, the position of the weak light-irradiated regions is important. When the interval between the respective weak light-irradiated regions is less than 1  $\mu\text{m}$ , the weak light-irradiated regions are in a continuous shape and irradiated portions are in a dot shape; and thus, advantages of regulating the liquid crystal regions of the present invention will be lost.

In contrast, when the interval between the respective weak light-irradiated regions is more than 50  $\mu\text{m}$ , portions where the intensity of UV-rays cannot be intercepted so as to regulate the liquid crystal regions are increased in number, and the number of liquid crystal regions with a random diameter as in the conventional example are formed, decreasing the advantages of the present example.

Thus, in the present example, the interval between the respective liquid crystal regions is in the range of 1  $\mu\text{m}$  to 50  $\mu\text{m}$ , and more preferably in the range of 5  $\mu\text{m}$  to 20  $\mu\text{m}$ .

A respective weak light-irradiated regions are not necessarily independent. The weak light-irradiated regions can be connected to each other at ends thereof. Any photomask with masking portions for decreasing the intensity of UV-rays which have the above-mentioned shape and orientation can be used.

A similar regularity is required for the photomask. In Example 1, a photomask satisfying the following conditions can be used:

Patterns are formed continuously or independently in a regular manner, and minimum repeating units of the patterns are within a circle having a diameter in the range of 1  $\mu\text{m}$  to 50  $\mu\text{m}$ . An interval from the center of one unit pattern to that of the adjacent unit pattern is in the range of 1  $\mu\text{m}$  to 50  $\mu\text{m}$ .

The photomask can be positioned either inside or outside the substrate. When the photomask is positioned

inside the substrate, a reflective mode (e.g., GH mode), etc. can be used. In this case, light is irradiated from the side of the substrate on which the photomask is not formed, and the photomask is used as a reflecting plate.

(Irradiation light)

It is preferred that the irradiation of light to the mixture is conducted by using light having the following light intensity distribution:

The light intensity of at least one portion of each pixel is 90% or less of the maximum illuminance in a circular area which corresponds to 10 times the pixel area and whose center is situated in the center of the pixel.

(A Liquid crystal material)

Examples of the liquid crystal used in the present invention include organic substances or organic mixtures which are in a liquid crystal state in the vicinity of an ordinary temperature, such as nematic liquid crystal (including liquid crystal for a dual frequency drive and liquid crystal with the anisotropy of dielectric constant  $\Delta\epsilon < 0$ ), cholesteric liquid crystal (in particular, liquid crystal having a selective reflection characteristic with respect to visible light), smectic liquid crystal, ferroelectric liquid crystal (e.g., SmC\*), and discotic liquid crystal. These liquid crystals can be mixed. In particular, nematic liquid crystal or nematic liquid crystal to which cholesteric liquid crystal is added is preferred in view of the properties thereof. More preferably, liquid crystal which is excellent in resistance to chemical combination reactivity due to the photopolymerization during the manufacturing is used. An example thereof includes liquid crystal having an inactive functional group such as a fluorine atom in its compound, e.g., ZLI-4801-000, ZLI-4801-001, and ZLI-4792 which are available from Merck & Co., Inc.

(A polymerizable material)

A polymerizable material is mixed with a liquid crystal material to form a mixture. Finally, the polymer thus obtained functions as a wall supporting two substrates and the liquid crystal regions. Thus, the selection thereof is important. The polymerizable material useful for the present example is a light-curable monomer. In addition, other polymerizable materials can be used. Examples of the light-curable monomer include acrylic acids and acrylic esters having a long chain alkyl group containing three or more carbons or an aromatic ring. Moreover, examples thereof include isobutyl acrylate, stearyl acrylate, lauryl acrylate, isoamyl acrylate, n-butyl-methacrylate, n-lauryl methacrylate, tridecyl methacrylate, 2-ethylhexyl acrylate, n-stearyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, and 2-phenoxyethyl methacrylate.

In order to increase the physical strength of the polymer, multi-functional material with two or more functional groups, such as bisphenol A dimethacrylate, bisphenol A diacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, trimethylol propane triacrylate, and tetramethylolmethane tetraacrylate can be used.

Moreover, a polymerizable material obtained by halogenating, in particular, by chlorinating or fluorinating the above-mentioned monomer can be used. Examples of this polymerizable material include 2,2,3,4,4,4-hexachlorobutyl methacrylate, 2,2,3,4,4,4-hexachlorobutyl methacrylate, 2,2,3,3-tetrachloropropyl methacrylate, 2,2,3,3-tetrachloropropyl methacrylate, perphlorooctyl methacrylate, perchlorooctylethyl methacrylate, perchlorooctylethyl acrylate, and perchlorooctylethyl acrylate.

The above-mentioned polymerizable material can be used alone or in combination of two or more kinds thereof. If required, chlorinated or fluorinated polymers or oligomers can be mixed with the above-mentioned monomer.

In the case where a thin film transistor (TFT) is used as a switching element, an electrical insulation property is required for a polymer as well as a liquid crystal material. Thus, a polymer which has a specific resistance of  $1 \times 10^{12} \Omega \cdot \text{cm}$  or more even in an uncured state is preferred.

In the production of a polymer dispersed liquid crystal display device by the conventional photopolymerization phase separation method, it is preferred that the liquid crystal material and the polymerizable material are combined so that a diameter of liquid crystal regions is larger than a dot diameter of a photomask used.

In the case where the combination of the polymerizable material and the liquid crystal material causes the diameter of the liquid crystal regions to be smaller than the dot diameter, this combination can be used by weakening the intensity of UV-rays or reducing the added amount of a photopolymerization initiator.

Hereinafter, applications for Example 1 will be described.

Application 1

Two substrates **12** and **13** were used. The substrate **12** was made of flint glass with ITO (a mixture containing indium oxide and tin oxide) with a thickness of 500 Angstroms (manufactured by Nippon Sheet Glass Co., Ltd.) functioning as the pixel electrodes **11**. The substrate **13** was also made of glass; and the photomask **14** with a dot pattern made of aluminum (having circles with a diameter of 10  $\mu\text{m}$ , the interval between the centers of adjacent circles being 15  $\mu\text{m}$  and circles being positioned in a matrix) was provided on one surface of the substrate **13** and the counter electrode **15** was formed on the other surface thereof by vapor-deposited ITO to a thickness of 500 Angstroms. The two substrates **12** and **13** faced each other with spacers having a diameter of 12  $\mu\text{m}$  sandwiched therebetween, whereby a cell was formed.

Then, 0.1 g of trimethylol propane trimethacrylate and 0.9 g of 2-ethylhexyl acrylate; and 4.0 g of a mixture in which ZLI-4792 (manufactured by Merck & Co., Inc.) was mixed with 0.03 g of a photopolymerization initiator Irgacure 184 (manufactured by CIBA-GEIGY Corporation) were homogeneously mixed. After that, the resulting mixture was inserted into the cell thus obtained. Then, the UV-rays **20** were irradiated through the photomask **14** to the cell by using a high-pressure mercury lamp (which can provide parallel rays) at an illuminance of 20 mW/cm<sup>2</sup> for two minutes to cure the polymerizable material, whereby a polymer dispersed liquid crystal display device was obtained. In the cell, the polymer walls **17** and the liquid crystal regions **16** regulated by the photomask **14** were formed in a regular manner.

The polymer dispersed liquid crystal display device was observed, revealing that the condition of uniformity was satisfied. More specifically, the interval **a** between the center of one liquid crystal region and the center of the adjacent liquid crystal region in a direction along the surface of the substrate was within a width of one pixel along this direction; and 95% of the intervals **a** satisfied the relationship:  $3b/2 > a > b/2$ , where **b** is an average of the intervals **a**.

The electro-optic characteristics of this polymer dispersed liquid crystal display device were as follows:

When light transmittance was increased by 10% of a value obtained by subtracting transmittance  $T_0$  under no voltage from the saturation transmittance  $T_{\text{sat}}$  under an excess voltage applied, an applied voltage  $V_{10}$  was 4.3 V. When light transmittance was increased by 90% of a value obtained by subtracting transmittance  $T_0$  under no voltage from a saturation transmittance  $T_{\text{sat}}$  under an excess voltage applied, an applied voltage  $V_{90}$  was 5.1 V. Thus, the drive voltage of Application 1 was lower than that of the conventional polymer dispersed liquid crystal display device, and had excellent agility ( $\alpha = V_{90}/V_{10} = 1.18$ ). Moreover, polarizing plates were provided on the upper and lower sides of the polymer dispersed liquid crystal display device so that each polarizing direction crossed each other at right angles (crossed Nicols). Because of this, when a voltage was applied, the liquid crystal display device was in a black state, and when a voltage was not applied, it was in a white state. Thus, a satisfactory black and white display was achieved.

Comparative Example 1

A polymer dispersed liquid crystal display device was manufactured in the same way as in Application 1 except that a glass substrate with ITO (flint glass with ITO having a thickness of 500 Angstroms, manufactured by Nippon Sheet Glass Co., Ltd.) was used in place of the substrate **13** with the photomask **14**.

The liquid crystal display device thus obtained was observed by using the SEM, revealing that the diameter and shape of the liquid crystal regions were not uniform. In this device, the interval **a** between the center of one liquid crystal region and the center of the adjacent liquid crystal region in a direction along the surface of the substrate was within a width of one pixel along this direction; and 65% of the intervals **a** satisfied the relationship:  $3b/2 > a > b/2$ , where **b** is an average of the intervals **a**. As to the electro-optic characteristics,  $V_{10}$  and  $V_{90}$  were 7.5 V and 13.7 V, respectively and  $\alpha = 1.83$ .

Application 2

In place of the glass substrates **12** and **13** used in Application 1, PET films with ITO having a thickness of 125  $\mu\text{m}$  were used. Spacers with a diameter of 12  $\mu\text{m}$  were dispersed on one PET film, and the other PET film was placed thereon to form a cell. The same material as that of Application 1 was injected into the cell. Then, a photomask **14** having the same dot pattern as that of Application 1 was placed so that a mask image was in contact with the PET film, and UV-rays were irradiated to the cell through the photomask **14** in the same way as in Application 1, whereby a polymer dispersed liquid crystal display device was obtained.

The polymer dispersed liquid crystal display device thus obtained was cut, and one substrate was peeled off from the other substrate in liquid nitrogen. After, the liquid crystal material was washed away with acetone, and a horizontal section of the polymer walls was observed by the SEM. As a result, it was revealed that uni-

formly aligned liquid crystal regions with almost the same size were formed having the same regularity as that of the dot pattern of the photomask 14. The interval  $a$  between the center of one liquid crystal region and the center of the adjacent liquid crystal region in a direction along the surface of the substrate was within a width of one pixel along this direction; and 97% of the intervals  $a$  satisfied the relationship:  $3b/2 > a > b/2$ , where  $b$  is an average of the intervals  $a$ . Moreover, as to the electro-optic characteristics,  $V_{10}$  and  $V_{90}$  were 4.6 V and 5.8 V, respectively. Thus, the liquid crystal display device having a lower drive voltage, compared with the conventional polymer dispersed liquid crystal display device and having excellent agility ( $\alpha = V_{90}/V_{10} = 1.26$ ) was obtained.

#### Comparative Example 2

A polymer dispersed liquid crystal display device was manufactured in the same way as in Application 2, except that UV-rays were irradiated without using the photomask 14. The shape of the polymer regions in the polymer dispersed liquid crystal display device thus obtained was not uniform. The interval  $a$  between the center of one liquid crystal region and the center of the adjacent liquid crystal region in a direction along the surface of the substrate was within a width of one pixel along this direction; and 67% of the intervals  $a$  satisfied the relationship:  $3b/2 > a > b/2$ , where  $b$  is an average of the intervals  $a$ . Moreover, as to the electro-optic characteristics,  $V_{10}$  and  $V_{90}$  were 7.7 V and 14.3 V, respectively and  $\alpha = 1.85$ .

As described above, in the case of Example 1, a polymer dispersed liquid crystal display device in which liquid crystal regions each having a uniform diameter are regularly aligned along a surface of a substrate can be manufactured with a good yield in a smaller number of steps.

In addition, a liquid crystal display device obtained by using the method of Example 1 has a performance comparable to the conventional liquid crystal display device (which is not polymer dispersed). Moreover, the number of liquid crystal regions in one pixel and the shape thereof can be freely varied, so that the regulation of the intensity of light scattering which occurs on the interfaces between the liquid crystal regions and the polymer walls, the adjustment of a drive voltage, the high precision of a screen, and the like are made possible, all of which cannot be achieved by the conventional polymer dispersed liquid crystal display device. Furthermore, since the diameter of the liquid crystal regions is uniform, the threshold value characteristic curve becomes steep, and a display with high precision and high contrast is made possible. In the case where a light-intercepting mask is provided as described above, the light scattering which occurs on the interfaces between the liquid crystal regions and the polymer walls can be prevented and contrast characteristics can be further improved. The liquid crystal display device obtained in Example 1 can be used in a simple matrix drive with high duty ratio. The liquid crystal display device obtained in Example 1 can be used, for example, in a surface display device of a projection TV, a personal computer, etc., a display plate, a window, a door, a wall, and the like utilizing shutter effects. In particular, the liquid crystal display device obtained in Example 1 can be used as a polymer dispersed liquid crystal display device of a direct viewing type.

#### Example 2

Example 2 is the case where the present invention is applied to a non light scattering type liquid crystal display device.

A method for manufacturing a liquid crystal display device according to Example 2 will be described with reference to Figures 2A and 2B.

First, as shown in Figure 2A, a substrate 1 and a counter substrate 3 face each other. A mixture 5 containing a liquid crystal material and a light-curable material is sealed between the two facing substrates 1 and 3. The substrate 1 is transparent, and pixel electrodes 2 are formed on the underside of the substrate 1. A counter electrode 4 is formed over the entire inner surface of the counter substrate 3.

On the substrate 1, a glass plate 6 on which a photomask 7 is formed is placed. The mixture 5 is irradiated with UV-rays 10 through the photomask 7. Consequently, as shown in Figure 2B, walls 8 formed of a polymer resin and liquid crystal regions 9 partitioned by the walls 8 are formed. In stronger UV-rays irradiated regions, a polymer is rapidly deposited due to the high polymerization rate, and liquid crystal molecules which are present together with the polymer are pushed out to weaker UV-rays irradiated regions. As a result, the liquid crystal regions 9 are formed in the weaker UV-rays irradiated regions. The liquid crystal regions 9 have flat portions in the vicinity of the substrates 1 and 3, the flat portions being parallel with the surfaces of the substrates 1 and 3.

In the liquid crystal display device of the present invention thus manufactured, the liquid crystal regions 9 are formed in regions which are covered with masking portions of the photomask 7; and the polymer walls 8 are formed in regions which are not covered with the masking portions of the photomask 7. That is to say,



the liquid crystal regions 9 and the polymer walls 8 are formed under the condition that they are clearly separated from each other.

5 The reason for providing the horizontal portions in the liquid crystal regions 9 is that boundaries between the liquid crystal regions 9 and the polymer walls 8 are positioned outside a pixel and incident light is allowed to pass through only the liquid crystal regions 9 which have less variation of refractive index in each portion thereof, thereby decreasing their light scattering ability. In this case, as the horizontal portions become larger, more effective results can be obtained.

10 Since the polymer walls 8 reach both of the substrates 1 and 3 (strictly speaking, the polymer walls 8 do not reach the surfaces of the substrates, since electrodes etc. are formed on the substrates) the substrates 1 and 3 are securely supported by the polymer walls 8, whereby shock resistance can be improved. Moreover, even though the liquid crystal display device is used under the condition that the device stands on end, a lower gap between the substrates 1 and 3 is prevented from being wider than an upper gap therebetween. In particular, the liquid crystal display device of the present example is effective in the case where film-shaped substrates are used.

15 The real shape of the liquid crystal regions formed in Example 2 can be observed and confirmed by peeling one of the two substrates from the other substrate, removing the liquid crystal molecules with a solvent, and by analyzing the polymer walls 8 with the SEM. Since some portions of the liquid crystal display device are likely to be damaged while samples for the SEM observation are formed, it is preferred that 20 liquid crystal regions which are most excellent in regularity among samples are selected to observe the polymer matrix.

20 Figure 3 shows a view obtained by observing the state, in which the polymer wall 8 and the liquid crystal regions 9 are divided by phase separation, by using a microscope. As is understood from this figure, the polymer wall 8 is not formed in a region to which UV-rays weakened by the photomask 7 is irradiated; and the polymer wall 8 is formed in a region to which UV-rays are irradiated and in the vicinity thereof. It is noted that 25 in some cases, small liquid crystal regions are formed in the polymer walls 8.

Hereinafter, the structure of each component applied to the present example and modified examples thereof will be described.

(A light regulating means such as a photomask)

30

The study of the inventors of the present invention revealed the following:

35 Among portions of a photomask for forming light-irradiated regions and weak light-irradiated regions, in the case where the masking portions for forming the weak light-irradiated regions respectively have an area of 30% or less of each pixel area, the liquid crystal regions also respectively have an area of 30% or less of each pixel area. This case is not practical since a number of interfaces between the liquid crystal regions and the polymer walls are present in one pixel, greatly decreasing contrast because of light scattering. Thus, in the present example, at least one liquid crystal region contained in one pixel has an area of 30% or more of each pixel area.

40 More specifically, in the present example, as shown in Figure 2B, the size of each liquid crystal region 9 is made almost the same size as that of the pixel electrode 2. In this structure, only one liquid crystal region 9 can be formed within one pixel, and the orientation direction of the liquid crystal regions 9 can be set by providing orientation films on the substrates 1 and 3. This structure is preferred in view of the ratio of aperture (i.e., a ratio of the total effective area of all the pixels to the area of the display area).

45 In the present example, it is preferred that the liquid crystal display regions 9 are regularly aligned along a surface of the substrate, i.e., with respect to each pixel. In this case, as shown in Figure 4, it is preferred that the position of each weak light-irradiated region for forming each liquid crystal region 9 is adjusted to an orientation pitch of pixels 9a, and one weak light-irradiated region is positioned in one pixel. Alternatively, as shown in Figure 5A, one weak light-irradiated region is positioned over two pixels 9a or over three or more pixels 9a. As shown in Figure 5B, it is possible that weak light-irradiated regions are formed over each column 50 of the pixels 9a. In addition, the masking portions of the photomask for forming the weak light-irradiated regions are not necessarily separated from each other completely, and can be connected to each other at the ends thereof, as long as the masking portions have the shape and orientation (described later) for effectively intercepting UV-rays (but not completely intercepting UV-rays).

55 Furthermore, as shown in Figure 6, in order to decrease the number of the interfaces in a pixel between the liquid crystal regions 9 and the polymer walls 8 which cause the light scattering, it is preferred that the weak light-irradiated regions larger than the pixel electrodes 2 are formed. In this case, a light regulating means which allows UV-rays to radiate to only the portions other than the pixels can be used. In particular, as the light regulating means, a photomask can be used, whereby the intensity of light scattering in the pixels is decreased and contrast of the liquid crystal display device can be improved.



Any shape of the masking portions can be used as long as the intensity of UV-rays in 30% or more of all of the pixels is decreased. In the present example, a masking portion corresponding to a circle, a square, a trapezoid, a hexagon, a rectangle, a diamond shape, a letter shape, a shape surrounded by a curved line(s) and/or a straight line(s) can be used, although it is not limited to these shapes. A configuration obtained by cutting a part of these shapes; a configuration obtained by the combination of the different shapes; a configuration obtained by the combination of the same shapes; and the like can be used. When the present invention is put into practical use, one or more of these shapes are selected. In order to improve uniformity of the liquid crystal regions, it is preferred to limit the configuration to one shape with the same size.

In the present example, another light regulating means can be used in place of a photomask. For example, a microlens, an interfering plate, etc. capable of forming a regular distribution of the intensity of UV-rays can be used. Such light regulating means can be provided inside or outside the liquid crystal display device, as long as strong UV-rays and weak UV-rays can be irradiated in a regular manner. In the case where a photomask is used, if a distance between the liquid crystal layer and the photomask is made large, an image is blurred due to the light passed through the photomask and weak light-irradiated regions become unclear, resulting in decreased advantages of the present invention. Thus, it is preferred that the photomask is placed as close as possible to the liquid crystal layer.

#### (Irradiation light)

UV-rays used in the present example are desirably parallel rays, although a light beam and line light can be used. In the case of a liquid crystal display device using ferroelectric liquid crystal, light with a slightly poorer degree of parallelization can be used. More specifically, in the case of the liquid crystal display device using ferroelectric liquid crystal, it is required to improve shock resistance. For that purpose, it is effective to provide smaller liquid crystal regions at the periphery of the liquid crystal regions as a buffer substance. Instead of using light with a slightly poorer degree of parallelization, a light regulating means such as a photomask having end portions which allow more light to pass therethrough toward the outside thereof can be used, or the photomask can be placed at a distance from a cell body. In the present example, ordinary light including UV-rays can be used.

According to the present example, the weak light-irradiated regions almost corresponding to required liquid crystal regions in terms of position are formed, whereby a polymerizable material can regularly be optically polymerized and uniform liquid crystal regions can regularly be positioned in a direction along the surface of the substrate.

#### (An optimum thickness of a liquid crystal layer)

An optimum thickness of a liquid crystal layer is varied depending upon the display mode.

#### (A method for injecting a mixture between substrates)

In the present example, two substrates are attached to each other by the conventional general method, and after that a mixture containing the liquid crystal material and the light-curable material is injected between the substrates. Alternatively, before the two substrates are attached to each other, the mixture is dropped or coated onto one substrate, and under this condition, UV-rays are irradiated to the substrate to cure the light-curable material. Then, the two substrates are attached to each other. The latter method has the advantage in that spacers and the like are not required for regulating the thickness of the liquid crystal layer.

Alternatively, an injection method shown in Figure 7 (a front view) and Figure 8 (a cross-sectional view) can be used. According to this method, in a cell in which two substrates 51 and 52 facing each other are sealed, at least two openings 52a and 52b are formed in the substrate 52. While air is taken out of one opening 52a, a mixture is injected through the other opening 52b into the cell by using an injector 53 shown in Figure 9. As to the position of the openings, one or more opening can be provided in one substrate and the remaining openings can be provided in a sealed portion. The air in the cell can be vacuumed through an opening from outside thereof. In this case, it is preferred that the degree of decompression be in the range of 200 Pa to atmospheric pressure in the opening to which a vacuum is applied. Moreover, it is also possible that while pressure is applied from one opening, a mixture is injected from that opening to which pressure is applied. In this case, it is preferred that the degree of pressure be in the range of atmospheric pressure to  $10^6$  Pa.

This injection method can be applied to Example 1.

(A method for an orientation treatment)

Examples of a method for an orientation treatment include a rubbing method in which after a polymer material such as polyimide and an inorganic material are coated onto a surface of a substrate, the resulting substrate is rubbed by using a cloth; a homeotropic method in which a surfactant compound with low surface tension is coated onto a substrate; and a diagonal orientation method in which  $\text{SiO}_2$  is vapor-deposited onto a substrate.

(An orientation film)

In the present example, substrates with orientation films can be used. In this case, as shown in Figures 10A and 10B, orientation films 8a and liquid crystal molecules in the liquid crystal regions 9 are in direct contact with each other, whereby the liquid crystal molecules can be oriented.

A preferred orientation film will be described in detail in Example 9.

(A polymerizable material)

A polymerizable material is mixed with a liquid crystal material to form a mixture. Finally, the polymer thus obtained functions as a wall supporting two substrates and the liquid crystal regions. Thus, the selection thereof is important. The polymerizable material useful for the present example is a light-curable monomer. In addition, other polymerizable materials can be used. Examples of the light-curable monomer include acrylic acids and acrylic esters having a long chain alkyl group containing three or more carbons or an aromatic ring. Moreover, examples thereof include isobutyl acrylate, stearyl acrylate, lauryl acrylate, isoamyl acrylate, n-butylmethacrylate, n-lauryl methacrylate, tridecyl methacrylate, 2-ethylhexyl acrylate, n-stearyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, and 2-phenoxyethyl methacrylate.

In order to increase the physical strength of the polymer, multi-functional materials with two or more functional groups, such as bisphenol A dimethacrylate, bisphenol A diacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, trimethylol propane triacrylate, and tetramethylolmethane tetra acrylate can be used.

Moreover, a polymerizable material obtained by halogenating, in particular, by chlorinating or fluorinating the above-mentioned monomer can be used. Examples of this polymerizable material include 2,2,3,4,4,4-hexaphlorobutyl methacrylate, 2,2,3,4,4, 4-hexachlorobutyl methacrylate, 2,2,3,3-tetraphloropropyl methacrylate, 2,2,3,3-tetraphloropropyl methacrylate, perphlorooctyl methacrylate, perchlorooctylethyl methacrylate, perphlorooctylethyl acrylate, and perchlorooctylethyl acrylate.

The above-mentioned polymerizable material can be used alone or in a combination of two or more kinds thereof. If required, chlorinated and/or fluorinated polymers or oligomers can be mixed with the above-mentioned monomer.

In the case where a thin film transistor (TFT) is used as a switching element, an electrical insulation property is required for a polymer as well as a liquid crystal material. Thus, a polymerizable material which has a specific resistance of  $1 \times 10^{12} \Omega \cdot \text{cm}$  or more even in an uncured state is preferred.

(A liquid crystal material)

Examples of the liquid crystal used in the present invention include organic substances or organic mixtures which are in a liquid crystal state in the vicinity of an ordinary temperature, such as nematic liquid crystal (including liquid crystal for a dual frequency drive and liquid crystal with anisotropy of dielectric constant  $\Delta\epsilon < 0$ ), cholesteric liquid crystal (in particular, liquid crystal having a selective reflection characteristic with respect to visible light), smectic liquid crystal, ferroelectric liquid crystal (e.g.,  $\text{SmC}^*$ ), and discotic liquid crystal.

As the ferroelectric liquid crystal, linear molecules having a hard core portion and an optically active portion in the molecules can be used. Moreover, it is also possible that a guest-host mode liquid crystal display device using the ferroelectric liquid crystal material to which a multi-color dye is added is manufactured, and this device is combined with one polarizing plate to form a liquid crystal display device. As a ferroelectric liquid crystal prepolymer, a compound obtained by binding one part of the above-mentioned ferroelectric liquid crystal with a polymerizable functional group can be used. Examples of the polymerizable functional group include an acrylate group, a methacrylate group, an epoxy group, etc. Examples of the ferroelectric liquid crystal prepolymer include compounds disclosed in Japanese Laid-Open Patent Publication Nos. 62-277412, 63-264629, and 63-280742. Moreover, a curable resin which is not liquid crystal can be added to liquid crystal to such a degree that the response speed of the liquid crystal display device is not deteriorated.

Two or more liquid crystal materials can be mixed. In particular, nematic liquid crystal or nematic liquid crystal to which cholesteric liquid crystal or a chiral agent is added is preferred in view of the properties thereof. Moreover, photopolymerization is involved during the manufacturing of liquid crystal regions, so that a liquid crystal material excellent in resistance to chemical combination reactivity without being modified during the polymerization is preferably used. An example thereof includes liquid crystal having an inactive functional group such as a fluorine atom in its compound, e.g., ZLI-4801-000, ZLI-4801-001, and ZLI-4792 which are available from Merck & Co., Inc.

#### (Conditions for forming liquid crystal regions)

It is difficult to separately form light scattering type and non light scattering type liquid crystal regions. In general, liquid crystal regions which have a diameter of less than 20  $\mu\text{m}$  in a cell and are uniformly formed in a pixel can be used in a liquid crystal display device suitable for a light scattering type. In contrast, liquid crystal regions which have large horizontal portions which are parallel with the substrates can be used in a liquid crystal display device suitable for a non light scattering type.

The size of liquid crystal regions depends upon the shape of the masking portions of a photomask, a degree of parallelization of light of a light irradiation device, and a photopolymerization rate, respectively. The shape of the masking portions is an important factor for determining the size of the liquid crystal regions. When the shape of the masking portions is determined, an outline of the liquid crystal regions is almost determined.

The degree of parallelization of light is a factor for determining whether light can exactly be irradiated to a mixture containing liquid crystal, a light-curable material, and a photopolymerization initiator, as in the form of the shape of the masking portions of the photomask. The degree of parallelization of light also influences the amount of light leaked from light-irradiated regions to weak light-irradiated regions. Because of such leaked light, the light-curable material present in the weak light-irradiated regions is cured before moving into the light-irradiated regions; as a result, small liquid crystal regions which are suitable for a light scattering type liquid crystal display device are formed in the weak light-irradiated regions.

In the case of a high photopolymerization rate, the light-curable material is cured even due to slightly leaked light, and consequently, polymer walls are formed in the weak light-irradiated regions. Examples of a factor for determining the photopolymerization rate include added amounts of the photopolymerization initiator, the intensity of light irradiation, the kind of the polymerizable material, and the like.

#### (A display mode)

The liquid crystal display device manufactured in the present example is sandwiched by two polarizing plates, whereby a liquid crystal display device of a TN mode, an STN mode, an ECB mode, and a guest-host mode (in which the drive voltage characteristic curve is steep); and a ferroelectric liquid crystal display device can be manufactured. One polarizing plate can be provided only on the side of one substrate. Namely, when a polarizing plane of light is changed by electrically regulating the orientation direction in liquid crystal which is obtained by adding a dichroic dye to ferroelectric liquid crystal, only one polarizing plate can be used.

#### (Ability for regulating the orientation of liquid crystal molecules)

In the case where light is irradiated to the mixture containing the liquid crystal molecules and the light-curable material under the condition that weak light is irradiated to some parts of the mixture as in the present invention, a thin polymer film is sometimes retained on the surface of the substrate even in the liquid crystal regions. Thus, the ability of the orientation films on the substrates is sometimes decreased. The liquid crystal molecules can be aligned depending upon the light irradiation conditions as in applications described later by completely removing the ability of the orientation films. More specifically, domains in the liquid crystal regions are aligned in a radial manner or a random manner, and when a voltage is applied, the liquid crystal molecules stand in almost the same way when seen from any direction. Thus, the refractive index no longer depends upon the direction in which the liquid crystal display device is seen, and the characteristics of the viewing angle can be improved. In this case, orientation films are not required, so that the number of manufacturing steps (coating of orientation films, rubbing treatment, washing, etc.) can greatly be reduced, which is industrially advantageous.

Liquid crystal molecules can be in homeotropic orientation in which the liquid crystal molecules stand on end with respect to the cell by using a homeotropic orientation film with a strong ability for regulating the orientation. When a voltage is applied to the liquid crystal display device using homeotropic orientation films, the liquid crystal molecules tilt toward each polymer wall at a certain angle due to the interaction between the liquid

crystal molecules and the polymer material. Thus, the same refractive index is obtained when seen from any direction, improving the characteristics of the viewing angle.

The following is also confirmed in the present example:

In the case where a liquid crystal material with a strong orientation ability, such as ferroelectric liquid crystal is used, the liquid crystal molecules in the material can be aligned along the orientation state of the substrate even in the present invention in which the ability for regulating the orientation of substrates is decreased.

(Others)

In the present example, a simple matrix drive system, an active drive system using a TFT, an MIM, etc. can be applied; however, the drive system is not limited thereto.

Moreover, in the liquid crystal display device of the present example, a color display can be performed by providing a color filter on a pixel.

Hereinafter, applications for Example 2 will be described.

### Application 3

A plurality of electrode lines formed of ITO with a thickness of 50 nm were formed on a PET film with a thickness of 0.25 mm. Substrates were formed, two PET films thus obtained being counted as one set. The width of the electrode line, the gap between the adjacent electrode lines, and the number of the electrode lines were 200  $\mu\text{m}$ , 50  $\mu\text{m}$ , and 20, respectively. Polyimide (SE150: manufactured by Nissan Chemical Industries Ltd.) was coated onto one set of substrates by a spin coating method, and the substrates were subjected to rubbing in one direction with a nylon cloth, whereby orientation films were formed.

The resulting two substrates were combined so that the electrode lines on each substrate crossed each other at right angles. A gap between the substrates were kept at a predetermined size by inserting spacers with a diameter of 6  $\mu\text{m}$  between the substrates, whereby a cell was formed.

A photomask was placed on the cell under the condition that masking portions of the photomask cover each pixel 9a as shown in Figure 4. A homogeneous mixture containing 0.1 g of trimethylol propane trimethacrylate, 0.9 g of 2-ethylhexyl acrylate, 4 g of a mixture in which 0.3% cholesteric nanonate (CN) was added to a ferroelectric liquid crystal material (ZLI-3700-000, manufactured by Merck & Co., Inc.), and 0.03g of a photopolymerization initiator (Irgacure 184, manufactured by CIBA-GEIGY Corporation) was injected into the cell.

Next, the mixture was irradiated with UV-rays through the photomask at an illuminance of 10 mW/cm<sup>2</sup> for 2 minutes by using a high-pressure mercury lamp which can provide parallel rays, whereby the polymerizable material in the mixture was cured.

The liquid crystal display device manufactured as described above was cut, and one substrate was peeled off from the other substrate. The liquid crystal material was washed away with acetone, and after that, the liquid crystal layer was observed by an SEM. As a result, it was confirmed that uniformly aligned liquid crystal regions having the same regularity as those of a dot pattern of the photomask and a pixel pattern and having almost the same size as that of the dot pattern were formed.

Moreover, polarizing plates were attached to another liquid crystal display device manufactured in the same way as the above so that the polarizing direction of the polarizing plates coincides with the orientation direction of the substrates, thereby obtaining a polymer matrix TN liquid crystal display device.

### Comparative Example 3

As a comparative example with respect to Application 3, a TN liquid crystal display device with a conventional structure was manufactured as follows:

Two glass plates with ITO (flint glass with ITO having a thickness of 500 Angstroms, manufactured by Nippon Sheet Glass Co., Ltd.) were used in place of the substrates of Application 3. A cell was formed in the same way as in Application 3, only the same liquid crystal material as that of Application 3 was injected into the cell, and polarizing plates were attached to the cell so that the polarizing direction of the polarizing plates coincided with the orientation direction of the substrate, whereby a liquid crystal display device was manufactured.

### Comparative Example 4

In addition, as a comparative example with respect to Application 3, a liquid crystal display device with a conventional structure was manufactured as follows:

A cell was formed in the same way as in Application 3. The same mixture containing the liquid crystal and

the light-curable material as that of Application 3 was injected into the cell, and after that, the cell was irradiated with UV-rays without a photomask, whereby a polymer dispersed TN liquid crystal display device was produced.

Table 1 shows contrast characteristics of the liquid crystal display device of Application 3 and of the liquid crystal display devices of Comparative Examples 3 and 4.

Table 1

Comparison of contrast characteristics			
	Application 3	Comparative Example 3	Comparative Example 4
Contrast	38	41	9

It is understood from Table 1 that the liquid crystal display device of Application 3 has an electro-optic characteristic comparable to that of Comparative Example 3. Compared with the conventional polymer dispersed TN liquid crystal display device of Comparative Example 4, the liquid crystal display device of Application 3 has higher contrast due to less light scattering in the pixels. Moreover, in the liquid crystal display device of Application 3, two substrates are securely supported by the polymer walls as described above, so that substrates formed of a PET film can be used. When other plastic films or glass substrates were used instead of the PET film, the same advantages were obtained.

#### Application 4

Cytop (manufactured by Asahi Glass Co., Ltd.) was coated onto the same substrate as that of Application 3 so that the Cytop had a thickness of 0.2  $\mu\text{m}$ . Next, spacers were dispersed on one substrate, and the other substrate was placed thereon to form a cell in the same way as in Application 3. Then, the same photomask as that of Application 3 was placed in the same way as in Application 3. A homogeneous mixture containing 0.1 g of trimethylol propane trimethacrylate, 0.9 g of lauryl acrylate, 4 g of a liquid crystal material (ZLI-4788-000, manufactured by Merck & Co., Inc.), and 0.03 g of a photopolymerization initiator (Irgacure 184, manufactured by CIBA-GEIGY Corporation) was injected into the cell.

Next, the cell was irradiated with UV-rays through the photomask at an illuminance of 10  $\text{mW}/\text{cm}^2$  for 2 minutes by using a high-pressure mercury lamp which can provide parallel rays, whereby the polymerizable material in the mixture was cured.

The liquid crystal display device manufactured as described above was cut, and one substrate was peeled off from the other substrate. The liquid crystal material was washed away with acetone, and after that, the liquid crystal layer was observed by an SEM. As a result, it was confirmed that uniformly aligned liquid crystal regions having the same regularity as those of a dot pattern of the photomask and a pixel pattern and having almost the same size as that of the dot pattern were formed.

Moreover, polarizing plates were attached to another liquid crystal display device manufactured in the same way as the above so that each polarizing direction thereof crossed each other at right angles, whereby a polymer dispersed ECB liquid crystal display device was manufactured.

As shown in Figure 11A, in an ordinary ECB liquid crystal display device, liquid crystal molecules  $\bullet$  are in a homeotropic orientation having a tilt angle of several degrees when no voltage is applied. Therefore, as shown in Figure 11B, when a voltage is applied, the liquid crystal molecules  $\bullet$  tilt in the same direction. As a result, the apparent refractive index is different depending upon direction of observation, and retardation ( $\Delta n \cdot d$ , where  $\Delta n$  is a birefringence of liquid crystal molecules and  $d$  is a thickness of a liquid crystal cell) is changed, causing an inversion phenomenon in which black and white are inverted depending upon the position of observation and nonuniform contrast. In contrast, in the case where the mixture containing the liquid crystal and the light-curable material is irradiated with light having an illuminance distribution, a thin polymer layer is formed between the substrate and the liquid crystal to decrease the ability of the orientation film on the substrate for regulating the orientation. However, it was confirmed that when a homeotropic orientation film with a strong ability for regulating the orientation was used as in Application 4, the liquid crystal molecules were in a homeotropic orientation. More specifically, it was observed that the liquid crystal molecules  $\bullet$  stood on end with respect to the cell as shown in Figure 12A. When a voltage is applied to the cell, as shown in Figure 12B, the liquid crystal molecules  $\bullet$  tilt toward each polymer wall due to the interaction between the liquid crystal and the polymer walls. Thus, the refractive index becomes almost the same, when seen from any direction with a certain angle from a vertical direction of the cell, greatly improving the characteristics of the viewing

angle.

#### Comparative Example 5

As a comparative example with respect to Application 4, an ECB liquid crystal display device with a conventional structure was manufactured as follows:

Two glass plates with ITO (flint glass with ITO having a thickness of 500 Angstroms, manufactured by Nippon Sheet Glass Co., Ltd.) were used instead of the substrates of Application 4. A cell was formed in the same way as in Application 4. The liquid crystal material (ZLI-4788-000) which was the same as that used in Application 4 was injected into the cell. Two polarizing plates were attached to the cell so that each polarizing direction thereof crossed each other at right angles, whereby a conventional liquid crystal display device was manufactured.

#### Comparative Example 6

As a comparative example with respect to Application 4, a liquid crystal display device was manufactured as follows:

A cell was formed in the same way as in Application 4. The same mixture containing the liquid crystal and the light-curable material as that of Application 4 was injected into the cell. Then, the cell was irradiated with UV-rays without a photomask in the same way as in Application 4, whereby a polymer dispersed ECB liquid crystal display device was manufactured.

Table 2 shows the contrast characteristic of the liquid crystal display device of Application 4 together with those of Comparative Examples 5 and 6.

Table 2

Comparison of contrast characteristics			
	Application 4	Comparative Example 5	Comparative Example 6
Contrast	32	35	8

It is understood from Table 2 that the liquid crystal display device of Application 4 has an electro-optic characteristic comparable to that of Comparative Example 5. Compared with the conventional polymer dispersed liquid crystal display device of Comparative Example 6, the liquid crystal display device of Application 4 has higher contrast due to less light scattering in pixels. As to the characteristics of the viewing angle, in Comparative Example 5, inversion phenomenon was caused when seen from various directions, and in Application 4, such phenomenon was not caused and a large viewing angle was obtained. Moreover, in the liquid crystal display device of Application 4, substrates formed of PET films can be used. When other plastic films or glass substrates were used instead of the PET film, the same advantages were obtained.

#### Application 5

ITO films with a thickness of about 1000 Angstroms were formed on two glass substrates by a vapor deposition method, and a plurality of electrode lines were provided in parallel on the substrates by a wet etching method. Polyimide orientation films with a thickness of about 500 Angstroms were coated onto surfaces of the substrates, on which the electrode lines were formed, by a spin coating method. The resulting substrates were baked at 190°C for one hour and subjected to a uniaxial rubbing treatment, whereby orientation films were formed thereon. In order to regulate cell thickness, silica beads with a diameter of 2  $\mu$ m were dispersed on the substrate as spacers, and two substrates were attached to each other, whereby a cell was formed.

It is noted that the rubbing treatment was conducted so as to obtain the same rubbing treated directions of the substrates, when the two surfaces of the substrates having the electrode lines faced each other so that the electrode lines crossed at right angles.

Next, a homogeneous mixture containing 0.80 g of ferroelectric liquid crystal composition (ZLI-4003, manufactured by Merck & Co., Inc.), 0.02 g of polyethylene glycol diacrylate (NK ESTER A-200, manufactured by Shin Nakamura Chemical Industrial Co., Ltd.) as a polymerizable material, and 0.18 g of lauryl acrylate (NK ESTER LA, Shin Nakamura Chemical Industrial Co., Ltd.) was injected between the substrates. This mixture is in a nematic phase state or an isotropic liquid phase state at an ordinary temperature. The phase transition

temperature of this mixture is shown below:

$\text{SmC}^* \leftarrow 25^\circ\text{C} \rightarrow \text{SmA} \leftarrow 31^\circ\text{C} \rightarrow \text{cholesteric phase} \leftarrow 35^\circ\text{C} \rightarrow \text{isotropic phase}$

Next, a photomask was placed on the cell in the same way as in Application 3. The mixture was irradiated with UV-rays through the photomask at an illuminance of 10 mW/cm<sup>2</sup> for 2 minutes by using a high-pressure mercury lamp which can provide parallel rays, under the condition that the mixture was in a nematic phase or an isotropic liquid phase. The polymerizable material was cured by this irradiation, and a phase separation occurred in the mixture.

The phase separation was observed by a microscope, revealing that the polymer walls 8 were not formed in regions which were not covered with masking portions of the photomask, and the polymer walls 8 were formed in regions to which the UV-rays were irradiated and in the vicinity thereof as shown in Figure 3.

Moreover, the observation of the cell by a polarizing microscope having crossed Nicols revealed the following:

Center portions of the liquid crystal regions were in an ordinary surface stabilized ferroelectric (SSF) type orientation in the rubbed direction of the substrate. The orientation was rapidly changed in the vicinity of the polymer walls to be in a homeotropic orientation. On the other hand, in the regions to which the UV-rays were irradiated, light scattering occurred.

In the case where the mixture containing the liquid crystal and the light-curable material was irradiated with light having an illuminance distribution as in Application 5, even though a horizontal orientation film with weak ability for regulating the orientation is used, the liquid crystal molecules can be aligned in the orientation direction of the substrate by using a liquid crystal material such as ferroelectric liquid crystal (FCL) excellent in regulating ability.

Furthermore, the ferroelectric liquid crystal cell thus manufactured was placed under a microscope having crossed Nicols and applied with a memory pulse. It was confirmed that in the liquid crystal regions to which weak light was irradiated, the same switching as that obtained in an ordinary SSF type cell was obtained. In addition, when quenching phases of the cell and a polarizing plate were aligned so that switching occurred between a complete quenching state and a light transmission state, it was observed that the light irradiated regions have brightness between on and off states due to the leakage of light caused by disturbance of the orientation of the liquid crystal molecules and due to light scattering, even under the condition that an electrical field was not applied.

When other plastic films or the like were used instead of the glass substrate, the same results as the above were obtained.

#### Comparative Example 7

As a comparative example with respect to Application 5, a liquid crystal display device was manufactured as follows:

A cell was formed in the same way as in Application 5. A liquid crystal material (ZLI-4003) was injected into the cell, followed by being sealed, whereby a liquid crystal display device was manufactured.

#### Comparative Example 8

A liquid crystal display device was manufactured in the same way as in Application 5 and by using the same materials as those of Application 5, except that a photomask was not used during the light irradiation step.

Table 3 shows the contrast characteristic of the liquid crystal display device of Application 5 together with those of the liquid crystal display devices of Comparative Examples 7 and 8.

Table 3

	Application 5	Comparative Example 7	Comparative Example 8
Contrast	35	40	8

It is understood from Table 3 that the liquid crystal display device of Application 5 has an electro-optic characteristic comparable to that of Comparative Example 7. Compared with the conventional liquid crystal display device of Comparative Example 8, the liquid crystal display device of Application 5 has higher contrast due to less light scattering in the pixels. Moreover, in the liquid crystal display device of Application 5, even when plastic films or the like were used, the same advantages were obtained.

In the liquid crystal display device of Comparative Example 8, when the mixture of the liquid crystal and the polymerizable material was irradiated with UV-rays, the polymerizable material was almost uniformly cured, whereby a phase separation was caused between the liquid crystal and the polymerizable material. When the portion where the phase separation occurred was observed by a microscope, it was revealed that the liquid crystal regions 9 were randomly dispersed in the polymer walls 8 almost over that portion as shown in Figure 13. Moreover, when this cell was observed by using a polarizing microscope having crossed Nicols, it was confirmed that light scattering occurred in the polymer walls 8 and center portions of the liquid crystal regions 9 were in nearly an SSF type orientation along the rubbed direction of the substrate, and the orientation of the liquid crystal molecules became more random toward the polymer walls 8.

The ferroelectric liquid crystal cell thus obtained was sandwiched by polarizing plates so that the polarizing directions thereof crossed each other at right angles and applied with a memory pulse, confirming that the same switching as that of an ordinary SSF type cell was conducted. However, in the case of a reverse switching, complete quenching was not obtained and the orientation seemed to be partially nonuniform. The inspection of this nonuniform portion by the polarizing microscope revealed that light scattered in the polymer walls 8, and light was leaked due to the disturbance of the orientation of the liquid crystal molecules in the vicinity of the polymer walls.

Table 4 shows the shock resistance of the liquid crystal display devices of Application 5, Comparative Examples 7 and 8. These results were obtained by applying a pressure of 5 kg/cm<sup>2</sup> to the respective liquid crystal display devices and observing the change in the orientation of the liquid crystal molecules thereof.

Table 4

Results of pressure test	
Application 5	The orientation of the liquid crystal molecules were slightly disturbed only in a pixel present in a boundary portion between the pressurized region and the non-pressurized region. No problem was caused in terms of practical use.
Comparative Example 7	The orientation of the liquid crystal molecules was disturbed from the pressured point up to the periphery thereof. A problem was caused in terms of practical use.
Comparative Example 8	The orientation was disturbed in a pixel in a boundary portion between the pressurized region and the non-pressurized region. A problem was caused in terms of practical use.

Table 5 shows the change of the orientation in the case where the above-mentioned three liquid crystal display devices were dropped from a height of 30 cm.

Table 5

Results of drop test	
Application 5	Distinct disturbance of the orientation was not acknowledged.
Comparative Example 7	The orientation was disturbed over the entire region.
Comparative Example 8	Distinct disturbance of the orientation was not acknowledged.

As is understood from these tables, in the case of Application 5, there are no problems in the pressure test and in the drop test. In the case of both of Comparative Examples 7 and 8, there are problems in the pressure test and/or in the drop test.

#### Application 6

Two substrates on which a plurality of electrode lines were formed and which were subjected to a rubbing treatment in the same way as in Application 5 were prepared. A homogeneous mixture containing 0.80 g of ferroelectric liquid crystal composition (ZLI-4003, manufactured by Merck & Co., Inc.), 0.02 g of polyethylene glycol acrylate as a polymerizable material (NK ESTER A-200, manufactured by Shin Nakamura Chemical In-



dustrial Co., Ltd.), 0.18 g of lauryl acrylate as a polymerizable material (NK ESTER LA, manufactured by Shin Nakamura Chemical Industrial Co., Ltd.) and silica beads with a diameter of 2  $\mu\text{m}$  was coated onto one of the substrates under the condition that the mixture was in a nematic phase state or in an isotropic liquid phase state at an ordinary temperature. Then, the two substrates were attached to each other in the same way as in Application 5, whereby a cell was formed. A phase transition temperature of the mixture is shown below:

$\text{SmC}^* \leftarrow 25^\circ\text{C} \rightarrow \text{SmA} \leftarrow 31^\circ\text{C} \rightarrow \text{cholesteric phase} \leftarrow 35^\circ\text{C} \rightarrow \text{isotropic phase}$

Next, a photomask was placed on the cell in the same way as in Application 5. The mixture was irradiated with UV-rays through the photomask under the same condition as that of Application 5, whereby the polymerizable material in the mixture was cured. As a result a phase separation occurred between the liquid crystal and the polymer.

The observation of the cured portion of the mixture revealed that the polymer walls were not formed in the regions which were not covered with the masking portions of the photomask and the polymer walls were formed in the light irradiated regions and in the vicinity thereof.

As described above, the liquid crystal display device of Application 6 was obtained by coating the mixture onto one of the glass substrates on which the electrodes and orientation films were formed under the condition that the mixture was in a nematic phase state or an isotropic liquid phase state and attaching both of the glass substrates. There was no disturbed orientation in the liquid crystal display device thus obtained. However, in the case where the two glass substrates having the electrodes and the orientation films were attached to each other, and then the mixture containing the liquid crystal and the polymerizable material was injected between the substrates under the condition that liquid crystal molecules were in a nematic state or an isotropic state, as described in Application 5, distinct disturbance of the orientation was observed by a microscope in the vicinity of the hole for injection and in the vicinity of the sealing.

In Example 2, one liquid crystal region was provided in one pixel or one liquid crystal region was formed in two or more pixels. The present invention is not limited thereto. For example, it is also possible in the present invention that at least one liquid crystal region is provided in one pixel and another one or more liquid crystal region or a part thereof is provided in the same pixel. This structure is effective for enlarging a screen by increasing the size of each pixel for the following reasons:

When a photomask which completely covers a large pixel, an unreacted polymerizable material present in a center of the pixel is polymerized due to the leaked light during the irradiation of light; as a result, a number of liquid crystal regions or polymer islands are formed (which become a source for light scattering). Thus, contrast is remarkably decreased. On the other hand, a plurality of weak light-irradiated regions are formed in a pixel so that the above-mentioned structure is obtained. In this case, masking portions of a photomask to be used become small and an unreacted polymerizable material does not remain in the center of the pixel, so that a number of liquid crystal regions or polymer islands are not formed. Thus, satisfactory contrast can be obtained. In particular, in the case where a longitudinal side of the pixel exceeds 200  $\mu\text{m}$ , this structure is effective. In the case where a longitudinal side of the pixel exceeds 200  $\mu\text{m}$ , the maximum diameter of each weak light-irradiated region is preferably in the range of 20 to 500  $\mu\text{m}$ , and more preferably in the range of 50 to 200  $\mu\text{m}$ . In the case where the maximum diameter is less than 20  $\mu\text{m}$ , contrast is remarkably decreased due to a number of polymer walls in the pixel. In the case where the maximum diameter is more than 500  $\mu\text{m}$ , a light-curable material present in the center of the pixel is not likely to move to the end of the pixel. Thus, the liquid crystal regions cannot be formed substantially corresponding to the shape of the masking portions of the photomask. As to the position of the weak light-irradiated regions, it is preferred that the weak light-irradiated regions are provided so as to make the maximum diameter thereof as small as possible.

### Example 3

Example 3 is a non light scattering type liquid crystal display device in which characteristics of the viewing angle and contrast are improved. The non light scattering type liquid crystal display device will be described by way of illustrating Applications.

### Application 7

ITO (mixture of indium oxide and tin oxide) with a thickness of 500 Angstroms was provided on a glass substrate (flint glass: 1.1 mm thickness). Then, polyimide (SE150, manufactured by Nissan Chemical Industries Ltd.) was coated onto the substrate by a spin coating method, whereby an orientation film was formed thereon. In this way, two substrates were formed.

Spacers with a diameter of 5  $\mu\text{m}$  were dispersed on one substrate, and the other substrate was placed thereon so that the gap therebetween was kept at a predetermined size, whereby a cell was formed.

A photomask 43 shown in Figure 14 having square masking portions 43a, each side being 200  $\mu\text{m}$  was placed on the cell thus formed. Each square masking portion 43a was provided with an interval of 50  $\mu\text{m}$ . In the cell, a homogeneous mixture containing 0.9 g of isobornyl methacrylate, 0.1 g of acrylate with two functional groups, i.e., a photopolymerizable compound (R-684, manufactured by Nippon Kayaku K.K.), 4 g of a mixture in which 0.3% by weight of a chiral agent (S-811, manufactured by Merck & Co., Inc.) was added to liquid crystal material (ZLI-4792, manufactured by Merck & Co., Inc.), and 0.02 g of a photopolymerization initiator (Irgacure 184, manufactured by CIBA-GEIGY Corporation) was injected.

The cell was irradiated with UV-rays by using a high-pressure mercury lamp which can provide parallel rays. This irradiation was conducted under the condition that one cycle (including one second irradiation at an illuminance of 15 mW/cm<sup>2</sup> and 30 seconds non-irradiation) was repeated 20 times and then the irradiation was continuously conducted for 5 minutes. Thus, the polymerizable material was cured.

The resulting cell was observed by a polarizing microscope, which revealed the followings:

As shown in Figure 24A, 24B, 24C or 24D, an outside liquid crystal region d' was formed. The respective outside liquid crystal regions d' were formed with the same regularity as that of a dot pattern of the photomask 43 (or a pixel), each region d' having almost the same size. Moreover, liquid crystal domains g in each outside liquid crystal region d' were oriented in an omnidirection on a surface parallel with the surface of the substrate, and an inside liquid crystal region d was formed being surrounded by each outside liquid crystal region d'.

Polarizing plates were attached to the resulting cell, thereby manufacturing a liquid crystal display device.

#### Comparative Example 9

As a comparative example with respect to Application 7, a cell was formed in the same way as in Application 7. Then, the same liquid crystal material (in which 0.3% of S-811 was added) was injected into the cell thus formed. Polarizing plates were attached to the cell so that each polarizing direction thereof was aligned with the orientation direction of the cell, whereby a conventional TN liquid crystal display device was manufactured.

#### Comparative Example 10

Moreover, as a comparative example with respect to Application 7, a cell was formed in the same way as in Application 7. In the cell thus formed, a mixture containing liquid crystal, a light-curable material, and a photopolymerization initiator was injected in the same way as in Application 7. Then, the cell was irradiated with UV-rays in the same way as in Application 7, except that a photomask was not used. The resulting cell was sandwiched by polarizing plates so that the polarizing directions of each polarizing plate crossed each other at right angles, whereby a conventional polymer dispersed liquid crystal display device was manufactured.

Table 6 shows the electro-optic characteristics of the cell of Application 7 together with those of the cells of Comparative Examples 9 and 10.

Table 6

Comparison of electro-optic characteristics			
	Application 7	Comparative Example 9	Comparative Example 10
Contrast	30	41	9
Inversion phenomenon in half tone	○	×	Δ

For the purpose of measuring contrast, a cell and polarizing plates were combined so as to obtain a normally white state, and contrast of the cell thus obtained was measured by a liquid crystal evaluation device (LC-5000, manufactured by Ohtsuka Denshi Co., Ltd.). It is noted that a measurement value was taken as a ratio of light transmittance  $T_0$  with respect to light transmittance  $T_{\text{sat}}$  ( $T_0/T_{\text{sat}}$ ), where the light transmittance  $T_0$  was obtained when a lens with a collecting angle of 24° from the vertical direction of the cell was used under no voltage applied, and the light transmittance  $T_{\text{sat}}$  was obtained when the above lens was used with a saturation voltage applied. In Table 6, a mark ○ shows a state in which inversion phenomenon hardly occurs; a mark × shows a state in which inversion phenomenon is easily observed; and a mark Δ shows a state in which inversion phenomenon is barely observed.

As is understood from Table 6, the liquid crystal display device of Application 7 has electrooptic characteristics comparable to those of the conventional TN liquid crystal display device of Comparative Example 9.

In particular, in Application 7, the inversion phenomenon caused by changing the viewing angle as seen in the TN liquid crystal display device in a half tone is not observed, and contrast obtained by observing in a direction with an angle of 40° from the vertical direction of the cell is hardly changed. Moreover, compared with the conventional polymer dispersed liquid crystal display device (Comparative Example 10), less light scattering occurs, increasing contrast. In Comparative Example 10, as shown in Figure 22 a great number of liquid crystal regions d were dispersed in one pixel and the diameter of each region is very small. Thus, the liquid crystal display device thus obtained was a light scattering type.

#### Application 8

A homogeneous mixture containing 0.9 g of isobornyl methacrylate, 0.1 g of acrylate with two functional groups, i.e., a photopolymerizable compound (R-684, manufactured by Nippon Kayaku K.K.), 4 g of a mixture in which 0.3% by weight of a chiral agent (S-811, manufactured by Merck & Co., Inc.) was added to a liquid crystal material (ZLI-4792, manufactured by Merck & Co., Inc.), and 0.02 g of a photopolymerization initiator (Irgacure 184, manufactured by CIBA-GEIGY Corporation) was injected into a cell manufactured in the same way as in Application 7.

The cell was covered with the photomask shown in Figure 14 and irradiated with UV-rays by using a high-pressure mercury lamp which can provide parallel rays at an illuminance of 15 mW/cm<sup>2</sup> for 5 minutes, whereby a polymerizable material was cured.

The cell thus obtained was observed by a polarizing microscope, which revealed the following:

As shown in Figure 25, a plurality of circular liquid crystal regions d2 were formed at the end portions of a weak light-irradiated region b and a plurality of circular liquid crystal regions d1 were formed surrounded by the liquid crystal regions d2. Each liquid crystal region d2 was divided into one to several circular liquid crystal domains, and the respective domains were formed in a radial manner. Each liquid crystal region d1 was also divided into one to several circular domains, and each domain was randomly oriented.

When a voltage is applied under this condition, the direction in which liquid crystal molecules stand is different depending upon each liquid crystal domain. Therefore, when the weak light-irradiated region is seen from an omnidirection with a predetermined angle from the vertical direction of the weak light-irradiated region, an apparent refractive index becomes almost constant. Thus, characteristics of the viewing angle in a half tone can be improved.

Polarizing plates were attached to both sides of the cell thus manufactured so that each polarizing angle of the polarizing plates crossed each other at right angles. The electro-optic characteristic of the cell is shown in Table 7.

Table 7

Comparison of electro-optic characteristics		
	Application 8	Application 9
Contrast	25	19
Inversion phenomenon in half tone	○	Δ

#### Application 9

A homogeneous mixture containing 0.9 g of isobornyl methacrylate, 0.1 g of acrylate with two functional groups, i.e., a photopolymerizable compound (R-684, manufactured by Nippon Kayaku K.K.), 4 g of a mixture in which 0.3% by weight of a chiral agent (S-811, manufactured by Merck & Co., Inc.) was added to a liquid crystal material (ZLI-4792, manufactured by Merck & Co., Inc.), and 0.12 g of a photopolymerization initiator (Irgacure 184, manufactured by CIBA-GEIGY Corporation) was injected into a cell manufactured in the same way as in Application 7.

The cell was covered with the photomask shown in Figure 14 and irradiated with UV-rays by using a high-pressure mercury lamp which can provide parallel rays at an illuminance of 45 mW/cm<sup>2</sup> for 5 minutes, whereby a polymerizable material was cured.

The cell thus obtained was observed by a polarizing microscope, which revealed the following:

As shown in Figure 23, a plurality of circular liquid crystal regions d were formed in a weak light-irradiated region b. Polarizing plates were attached to both sides of the cell thus manufactured so that each polarizing

angle of the polarizing plates crossed each other at right angles. The electro-optic characteristic of the cell is shown in Table 7.

It is understood from the comparison of Applications 7, 8, and 9 based on Tables 6 and 7 that the inversion phenomenon in a half tone in the liquid crystal regions shown in Figure 25 of Application 8 is satisfactory to the same degree as that of Application 7, where the liquid crystal domains of the outside liquid crystal region are formed in a radial manner so as to surround another liquid crystal region; however, contrast is slightly less satisfactory than that of Application 7. Application 9 has a structure as shown in Figure 23, so that the inversion phenomenon occurs in a half tone and contrast is decreased.

In Applications 7 to 9, UV-rays were irradiated at an illuminance in the range of 15 mW/cm<sup>2</sup> of 45 mW/cm<sup>2</sup> by using a high-pressure mercury lamp. The conditions for irradiation of UV-rays are different depending upon the composition of a mixture of liquid crystal and a polymerizable material and are not particularly limited. However, in order to allow liquid crystal regions to sufficiently grow and to prevent damage to a liquid crystal material by UV-rays, the illuminance is preferably 60 mW/cm<sup>2</sup> (measured at 365 nm) or less.

The reason why a pulse irradiation is conducted at a cycle including one second irradiation and 30 seconds non-irradiation in Application 7 is as follows:

In the case where a mixture containing liquid crystal and a light-curable material is irradiated with light having an illuminance distribution, the light-curable material in light-irradiated regions reacts to form the cores of the polymer walls. Then, the concentration of the light-curable material in the light-irradiated region is decreased and the concentration gradient of the light-curable material is formed. As a result, an unreacted light-curable material in weak light-irradiated regions move to gather in the light-irradiated regions along the concentration gradient, whereby the unreacted light-curable material moved into the light-irradiated regions are polymerized to form polymer walls. At this time, in the case where the light-curable material has a high polymerization rate, the light-curable material in the weak light-irradiated regions is polymerized due to light leaked from the light-irradiated regions, before the light-curable material reaches the light-irradiated regions. Therefore, even in the weak light-irradiated regions, a plurality of liquid crystal regions are formed. If these liquid crystal regions are extremely small (e.g., 20  $\mu$ m or less), light is scattered at interfaces between the polymer walls and the liquid crystal regions, resulting in decreased contrast. For this reason, the extremely small liquid crystal regions are not preferred. In order to avoid this, the polymerization rate is made low, whereby the light-curable material in the weak light-irradiated regions can reach the light-irradiated regions completely, and a phase separation between the liquid crystal regions and the polymer walls can be made clear. This means that each pixel in the liquid crystal display device is almost covered with the liquid crystal regions to improve contrast.

In addition, as a method for making the phase separation clear, the light-curable material in the weak light-irradiated regions is allowed to be sufficiently moved into the light-irradiated regions under a non-irradiation condition by using light in a pulse state, whereby liquid crystal regions can be formed without forming small liquid crystal regions in the weak light-irradiated regions.

It is preferred to conduct a pulse irradiation for 5 seconds or less during which the polymerizable material is not sufficiently cured, with an interval of 30 seconds or more. In this pulse irradiation, liquid crystal domains can be in a random orientation instead of an omnidirectional orientation by regulating the polymerizable material and irradiation conditions.

#### Application 10

Application 10 is the case where a photopolymerization reaction is suppressed, a phase separation between liquid crystal molecules and a polymerizable material is made clear, and liquid crystal regions are formed so as to correspond to the shape of the masking portions of a photomask. In order to suppress a photopolymerization reaction, it is preferred that a photopolymerization suppressor be added.

ITO (mixture of indium oxide and tin oxide) with a thickness of 500 Angstroms was provided on a glass substrate (flint glass: 1.1 mm thickness). Spacers (micropearl, manufactured by Sekisui Fine Chemical Co., Ltd.) with a diameter of 5  $\mu$ m were dispersed on one substrate, and the other substrate was placed thereon so as to keep a gap therebetween, whereby a cell was formed.

The photomask 43 shown in Figure 14 having squares, each side being 200  $\mu$ m and each square being formed in a pitch of 250  $\mu$ m was placed on the cell thus formed. In the cell, a homogeneous mixture containing 0.85 g of isobornyl methacrylate, 0.1 g of acrylate with two functional groups, i.e., a photopolymerizable compound (R-684, manufactured by Nippon Kayaku K.K.), 0.05 g of styrene as a photopolymerization suppressor, 4 g of a mixture in which 0.3% by weight of a chiral agent (S-811, manufactured by Merck & Co., Inc.) was added to a liquid crystal material (ZLI-4792, manufactured by Merck & Co., Inc.), and 0.02 g of a photopolymerization initiator (Irgacure 651, manufactured by CIBA-GEIGY Corporation) was injected.

The cell was continuously irradiated with UV-rays from the side of a dot pattern of the photomask 43 by using a high-pressure mercury lamp which can provide parallel rays at an illuminance of 15 mW/cm<sup>2</sup> (measured at 356 nm) for 5 minutes.

5 The cell thus formed was observed by a polarizing microscope, which revealed the following:

Liquid crystal regions were uniformly formed with the same regularity as that of the dot pattern (or a pixel), each region having almost the same size. Moreover, liquid crystal domains in the liquid crystal regions were oriented in an omnidirection. Polarizing plates were attached to the upper and lower sides of the cell to manufacture a liquid crystal display device.

10

#### Comparative Example 11

As a comparative example with respect to Application 10, a liquid crystal display device was manufactured as follows:

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A cell was formed in the same way as in Application 10, and a mixture containing liquid crystal, a light-curable material, a photopolymerization initiator, which was the same as that of Application 10, was injected into the cell. The resulting cell was irradiated with light under the same conditions as those of Application 10. Polarizing plates were attached to the cell thus formed so that each polarizing angle crossed each other at right angles, whereby a conventional polymer dispersed liquid crystal display device in which the cell was sandwiched by the polarizing plates was manufactured.

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#### Comparative Example 12

Moreover, as a comparative example with respect to Application 10, a liquid crystal display device was manufactured as follows:

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First, polyimide (SE150, manufactured by Nissan Chemical Co., Ltd.) was coated onto a substrate which was the same as that of Application 10 by a spin coating method. The substrate was subjected to a uniaxial rubbing treatment by using a nylon cloth. Two substrates which were treated in this way were attached to each other at right angles so that each rubbing direction crossed the other. Spacers (micropearl, manufactured by Sekisui Fine Chemical Co., Ltd.) with a diameter of 5  $\mu$ m were dispersed on one substrate, and the other substrate was formed thereon so as to keep a gap therebetween, whereby a cell was formed. Then, a mixture in which 0.3% by weight of a chiral agent (S-811, manufactured by Merck & Co., Inc.) was added to a liquid crystal material (ZLI-4792, manufactured by Merck & Co., Inc.) was injected into the cell. Moreover, polarizing plates were attached to the cell so that the polarizing directions thereof coincided with the orientation direction of liquid crystal molecules in the cell, whereby a conventional TN liquid crystal display device was manufactured.

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Table 8 shows the electro-optic characteristic of the display device of Application 10 together with those of the display devices of Comparative Examples 11 and 12.

Table 8

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Comparison of electro-optic characteristics			
	Application 10	Comparative Example 11	Comparative Example 12
Contrast	35	9	41
Inversion phenomenon in a half tone	○	Δ	×

45

For the purpose of measuring contrast, a cell and polarizing plates were combined so as to obtain a normally white state, and contrast of the cell thus obtained was measured by a liquid crystal evaluation device (LC-5000, manufactured by Ohtsuka Denshi Co., Ltd.). It is noted that the measurement value was taken as a ratio of light transmittance  $T_0$  with respect to light transmittance  $T_{sat}$  ( $T_0/T_{sat}$ ), where the light transmittance  $T_0$  was obtained when a lens with a collecting angle of 24° from the vertical direction with respect to the cell was used under no voltage applied, and the light transmittance  $T_{sat}$  was obtained when the above lens was used with a saturation voltage applied. In Table 8, a mark ○ shows a state in which inversion phenomenon hardly occurs; a mark × shows a state in which inversion phenomenon is easily observed; and a mark Δ shows a state in which inversion phenomenon is barely observed.

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As is understood from Table 8, the liquid crystal display device of Application 10 has an electro-optic characteristic comparable to that of the conventional TN liquid crystal display device of Comparative Example 12.

In particular, in Application 10, the inversion phenomenon caused by changing the viewing angle as seen in the TN liquid crystal display device in a half tone is not observed, and the contrast obtained by observing in a direction with an angle of 40° from the vertical direction with respect to the cell is hardly changed. Moreover, compared with the conventional polymer dispersed liquid crystal display device (Comparative Example 11), less light scattering occurs, increasing contrast.

Moreover, in Application 8, the liquid crystal regions shown in Figure 25 were obtained without using a photopolymerization suppressor. In Application 10 using a photopolymerization suppressor, the liquid crystal regions as shown in Figure 26A, 26B, 26C, or 26D were obtained. Thus, the liquid crystal display device in Application 10 is excellent in contrast.

The above-mentioned photopolymerization suppressor is a compound capable of decreasing the photopolymerization rate by being added to the polymerizable material to be used. Examples of the photopolymerization suppressor include polymerizable compounds which have lower reactivity than acrylate and methacrylate and which have a Q value of 0.8 or more; such as styrene (Q = 1), parachlorostyrene (Q = 1.03), *a*-methylstyrene (Q = 0.98), and butadiene (Q = 2.39), where Q represents the resonance stability of a monomer in a radical polymerization. When a monomer has a larger value of Q, a radical to be generated is likely to be stabilized due to resonance effects, decreasing the radical polymerization rate. In the present invention, when a polymerization reaction is slow, the phase separation rate between the liquid crystal and the polymerizable material becomes lower. As a result, liquid crystal regions to be formed become large and almost the same size as that of masking portions of a photomask. This is preferred since contrast is improved. In addition, it is preferred to use a radical catcher such as a *p*-quinone derivative (e.g., *p*-quinone, *p*-chloroquinone, *p*-methylquinone), 2,2-diphenyl-1-picrylhydrazyl (DPPH), aromatic nitro compounds, and nitroso compounds (e.g., nitrobenzene, nitrotoluene, aniline, nitrosodimethylaniline).

The added amount of photopolymerization suppressor is varied depending upon its effects, and there is no particular limitation thereto in the present invention. However, it is preferred to add the photopolymerization suppressor in such a manner that when a change of photopolymerization reaction heat of a mixture of a light-curable material, a photopolymerization initiator (Irgacure 651, 0.3% added) and a photopolymerization suppressor is observed at an illuminance of 100 mW/cm<sup>2</sup> (measured at 365 nm), 25°C by a photodifferential scanning calorimeter (photo DSC: PDC121, manufactured by Seiko Instruments & Electronics Ltd.), the peak of the reaction heat lasts for 20 seconds or more. When the peak value is 20 seconds or less, liquid crystal regions do not sufficiently grow and polymer walls are partially formed within weak light-irradiated regions of the photomask, leading to a decrease in contrast.

Examples of the liquid crystal include organic mixtures exhibiting a liquid crystal state in the vicinity of an ordinary temperature, e.g., nematic liquid crystal (including liquid crystal for a dual frequency drive and liquid crystal with dielectric anisotropy of dielectric constant  $\Delta\epsilon < 0$ ), cholesteric liquid crystal (in particular, liquid crystal having selective reflection characteristics with respect to visible light), smectic liquid crystal, ferroelectric liquid crystal, and discotic liquid crystal. These liquid crystals can be mixed. In particular, nematic liquid crystal, cholesteric liquid crystal, or nematic liquid crystal to which a chiral agent is added are preferred in terms of the characteristics thereof. Considering problems of coloring caused by hysteresis, uniformity, and  $d\Delta n$  (retardation), cholesteric liquid crystal, nematic liquid crystal to which a chiral agent having a helical pitch of 10  $\mu\text{m}$  or more is added is preferred. Moreover, liquid crystal which is excellent in resistance to chemical reaction is preferred since a photopolymerization reaction is involved in manufacturing. More specifically, liquid crystal which has a functional group such as a fluorine atom in a compound is preferred. Examples thereof include ZLI-4801-000, ZLI-4801-001, ZLI-4792 (manufactured by Merck & Co., Inc.).

In the combination of the liquid crystal material and the polymer material, it is preferred that the diameter of a liquid crystal region formed becomes larger than the dot diameter of a photomask to be used in the present invention, when a polymer dispersed liquid crystal display device is manufactured by a conventional photopolymerization phase separation method. Even though the diameter of a liquid crystal region becomes smaller than a dot diameter of a photomask in a certain combination of the liquid crystal material and the polymerizable material, this combination can be used by decreasing the intensity of UV-rays, suppressing the added amount of the photopolymerization initiator, etc.

The mixed ratio of the liquid crystal material and the polymerizable material is preferably in the range of 60:40 to 95:5 by weight. When the polymerizable material exceeds the ratio of 60:40, regions which change with respect to a voltage are decreased, resulting in poor contrast. When the polymerizable material is less than the ratio of 95:5, it becomes difficult to form polymer walls sufficiently, and moreover, the  $T_{N-1}$  point of the mixture of the liquid crystal material and the polymerizable material becomes higher, resulting in difficulty for the vacuum injection of the mixture into the cell.

The added amount of the photopolymerization initiator is preferably in the range of 3 to 0.01% by weight based on the weight of the mixture of the liquid crystal material and the polymerizable material. When the add-

ed amount exceeds 3% by weight, the photopolymerization rate is too high to make the liquid crystal region large, decreasing an electrical holding ratio required for driving a TFT. When the added amount is less than 0.01% by weight, a sufficient photopolymerization reaction does not occur, and thus, polymer walls cannot be formed.

#### Application 11

As in Application 8, a liquid crystal display device, in which liquid crystal regions were partitioned by polymer walls, was manufactured by using the same substrate and materials as those of Application 10. In Application 11, a photomask 44 as shown in Figure 15 having a light transmission hole 44b in each masking portion 44a thereof and light transmission slit 44c formed in a broken line shape from the hole 44b toward four corners of the masking portion 44a was used.

The cell obtained was observed by a polarizing microscope, revealing the following:

As shown in Figure 27, in the center of each liquid crystal region d with regularity, there was a polymer region i in an island shape. In the liquid crystal region d, liquid crystal domains g were formed in a radial manner. The contrast measured in a vertical direction with respect to the cell was 29; and the contrast measured at an angle of 45° from the vertical direction of the cell in an omnidirection was in the range of 21 to 25. In a conventional TN cell, inversion phenomenon was obtained in a direction of a stigmatic angle, remarkably decreasing the display quality.

The liquid crystal display device, in which the liquid crystal regions are partitioned by the polymer walls and quasi-solidified, has the same function as that of a conventionally used liquid crystal display device (TN, STN, ECB, ferroelectric liquid crystal display devices, etc.) which has a high contrast and a steep drive voltage characteristic curve, and in which the cell is sandwiched by two polarizing plates. The liquid crystal display device of the present invention can be driven by a simple matrix drive method, an active drive method using a TFT or an MIM. The present invention is not particularly limited thereto.

#### Application 12

Application 12 is the case where a liquid crystal display device with a large screen is provided by aligning liquid crystal molecules in an omnidirection or in a random direction.

Hereinafter a method for manufacturing a liquid crystal display device of Application 12 will be described.

First, ITO (a mixture of indium oxide and tin oxide) with a thickness of 500 Angstroms was provided on a glass substrate (flint glass: 1.1 mm thickness). Then, polyimide (SE150, manufactured by Nissan Chemical Industries Ltd.) was coated onto the glass substrate by a spin coating method, whereby an orientation film was formed thereon. In this way, two substrates were formed.

Spacers with a diameter of 5  $\mu\text{m}$  were dispersed on one substrate, and the other substrate was placed thereon so as to keep a predetermined gap therebetween, whereby a cell was formed.

Then, a photomask 44 having a circular light transmission hole 44b with a diameter of 25  $\mu\text{m}$  in the center of each masking portion 44a as shown in Figure 16 was placed on the cell thus formed. In the cell, a homogeneous mixture containing 0.9 g of isobornyl methacrylate, 0.1 g of acrylate with two functional groups, i.e., a photopolymerizable compound (R-684, manufactured by Nippon Kayaku K.K.), 4 g of a mixture in which 0.3% by weight of a chiral agent (S-811, manufactured by Merck & Co., Inc.) was added to a liquid crystal material (ZLI-4792, manufactured by Merck & Co., Inc.), and 0.02 g of a photopolymerization initiator (Irgacure 184, manufactured by CIBA-GEIGY Corporation) was injected.

Next, the cell was continuously irradiated with UV-rays at an illuminance of 15 mW/cm<sup>2</sup> for 5 minutes by using a high-pressure mercury lamp which can provide parallel rays, whereby the polymerizable material was cured.

The resulting cell was observed by a polarizing microscope, which revealed the following:

As shown in Figure 27, in the center of each liquid crystal region d with regularity, there was a polymer region i in an island shape. In the liquid crystal region d, liquid crystal domains g were formed in a radial manner. The contrast measured in a vertical direction with respect to the cell was 28; and the contrast measured at an angle of 45° from the vertical direction of the cell in an omnidirection was in the range of 21 to 25. In a conventional TN cell, inversion phenomenon was obtained in a direction of a stigmatic angle, remarkably decreasing the display quality.

As described in Applications 11 and 12, when light irradiation is conducted by using a photomask having a light transmission hole in the center of each masking portion, a decrease in contrast due to light scattering can be prevented by aligning liquid crystal molecules in liquid crystal regions in an omnidirection, suppressing viewing angle dependency in a half tone, and letting the liquid crystal regions cover almost the entire pixel.

Moreover, a liquid crystal display device obtained by using this type of photomask can be utilized for a large screen and used as a liquid crystal display device required to have less viewing angle dependency. Thus, its application range is remarkably wide. Its application range covers a liquid crystal TV, a display device for a video camera (liquid crystal viewcam, manufactured by Sharp K.K.), eyeglasses-type liquid crystal display device for virtual reality, and a liquid crystal display device for vehicles. In the case where an area of a masking portion is very large, a plurality of light transmission holes can be provided, and one of the transmission holes is not necessarily positioned in the center of the masking portion. What is important is that almost all of the weak light-irradiated regions become liquid crystal regions and the liquid crystal molecules therein are aligned in a radial manner.

The technique of Example 3 can be applied to the case where two or more liquid crystal regions are formed in one pixel. Figure 17 shows this application. In Figure 17, the reference mark **b** denotes a pixel or a masking portion of a photomask, **c** an open portion of the photomask, **d** a liquid crystal region, and **e** liquid crystal molecules.

In Example 3, each item described in Example 2, such as the Light regulating means such as a photomask, Irradiation of light, etc. can be applied in the same way.

#### Example 4

In addition to the structure of Example 3, Example 4 is the case where a plurality of liquid crystal molecules **j** in a liquid crystal region **d** are aligned in a helical manner around a helical axis **k** which is nearly vertical with respect to a surface of a substrate as shown in Figure 28A. In this case, a liquid crystal material in which cholesteric liquid crystal, a chiral agent, or the like added to the nematic liquid crystal is used. Examples of the chiral agent include S-811, R-811, and CE12.

For example, when nematic liquid crystal (in particular, liquid crystal having a helical pitch) is used, the characteristics thereof are changed depending upon its helical pitch.

(1) In the case of a helical pitch of more than 100  $\mu\text{m}$ , the observation by a polarizing microscope reveals that as shown in Figures 29A and 29B, liquid crystal molecules are aligned in a liquid crystal region **d** in parallel with the substrate and orientation planes of the liquid crystal are hardly twisted. Namely, the liquid crystal molecules are in a nearly homogeneous orientation. In this case, when the cell is sandwiched by polarizing plates so that each polarizing direction crosses the other at right angles (crossed Nicols), light is transmitted through the cell only influenced by the effects of birefringence of the liquid crystal. Thus, the amount of light transmitted therethrough is small. Moreover, the difference of refractive index at an interface between the polymer wall and the liquid crystal region **d** becomes large under no applied voltage.

Therefore, when seen at a position with an angle from a vertical direction with respect to the cell, the interface between the polymer wall and the liquid crystal region **d** is revealed, resulting in a rough display. (2) In the case of a helical pitch of 15  $\mu\text{m}$  to 100  $\mu\text{m}$ , the observation by a polarizing microscope reveals that as shown in Figures 28A, 28B, and 28C, liquid crystal molecules are aligned in parallel with the substrate, twisted with each other, and have an orientation state in which the liquid crystal molecules on the upper and lower substrates are twisted (nearly in a TN orientation). In this case, light incident upon the cell is optically rotated by the twisted molecules, so that the incident light passes through the polarizing plates under crossed Nicols. Thus, the amount of light passed through the cell is increased. Moreover, the liquid crystal molecules at the interfaces between the liquid crystal regions and the polymer walls are aligned in parallel with the substrate, but randomly aligned within each interface. Therefore, when seen at a position with an angle from the vertical direction with respect to the cell, the interfaces between the liquid crystal regions and the polymer walls are hardly revealed, resulting in an improved display quality without roughness.

(3) In the case of a helical pitch of less than 15  $\mu\text{m}$ , the observation by a polarizing microscope reveals that as shown in Figures 30A and 30B, minute stripe patterns are generated in liquid crystal regions since a helical axis of the liquid crystal molecules is tilted from a vertical plane with respect to the cell. In an orientation state in which the helical axis lies down, only part of the liquid crystal molecules stands in the vertical direction of the cell, decreasing light transmittance.

As described above, in Example 4, the helical pitch is preferably in the range of 15  $\mu\text{m}$  to 100  $\mu\text{m}$ . More preferably, in view of light transmittance and roughness of a display, the helical pitch is in the range of 25  $\mu\text{m}$  to 75  $\mu\text{m}$ .

#### Applications 13, 14, 15 and 16

Two transparent electrode substrates with ITO were attached to each other so as to have a cell thickness



of 5.5  $\mu\text{m}$ . A mixture containing 0.1 g of R-684, 0.05 g of styrene, 0.85 g of isobornyl methacrylate, 4 g of a liquid crystal material (ZLI-4792), and 0.02 g of a photopolymerization initiator (Irgacure 651) was injected into the cell thus obtained. In the liquid crystal material, 0.3% by weight of S-811 (Application 13), 0.6% by weight of S-811 (Application 14), 0.9% by weight of S-811 (Application 15), and 1.2% by weight of S-811 (Application 16) were added as a chiral agent, respectively. The mixture was heated to 40°C so as to obtain a homogeneously mixed state. Then, a photomask having square masking portions each side of which is 200  $\mu\text{m}$ , the masking portions being provided in a matrix with an interval of 50  $\mu\text{m}$  from each other, was placed on the cell. The cell was irradiated with UV-rays through the photomask by using a high-pressure mercury lamp at an illuminance of 14 mW/cm<sup>2</sup> under the condition that a cycle including one second irradiation and 29 seconds non-irradiation was repeated 20 times and then continuously irradiated for 5 minutes. Moreover, the cell was irradiated for 5 minutes without the photomask. Polarizing plates were attached to the upper and lower sides of the resulting cell so that each polarizing direction crossed the other at right angles.

#### Comparative Examples 13 and 14

As comparative examples with respect to Applications 13, 14, 15 and 16, liquid crystal display devices were manufactured as follows:

Cells were formed in the same way as in Applications 13, 14, 15 and 16. Then, a mixture containing 4 g of a liquid crystal material (ZLI-4792), and 0.02 g of a photopolymerization initiator (Irgacure 651) was injected into each cell. In the liquid crystal material, 0% by weight of S-811 (Comparative Example 13) and 1.5% by weight of S-811 (Comparative Example 14) were added as a chiral agent, respectively.

Table 9 shows electro-optic characteristics of the liquid crystal display devices of Applications 13, 14, 15 and 16; and Comparative Examples 13 and 14. A drive voltage ( $V_{th}$ ) represents a voltage when light transmittance is changed by 10%; and  $T_0$  represents light transmittance under no applied voltage, (where light transmittance obtained when two polarizing plates are attached so that each polarizing plate is aligned is taken as 100%). A helical pitch of the liquid crystal material was measured by using a wedge-shaped cell.

Table 9

	Comparative Example 13	Application 13	Application 14	Application 15	Application 16	Comparative Example 14
Helical pitch ( $\mu\text{m}$ )	--	75	38	26	17	13
Drive voltage $V_{th}$ (V)	3.2	2.7	1.9	1.1	1.3	1.8
Light transmittance $T_0$ (%)	18	35	40	32	25	12

As is understood from Table 9, when the helical pitch of the liquid crystal material is in the range of 15  $\mu\text{m}$  to 100  $\mu\text{m}$ , a bright display with improved light transmittance is made possible. The helical pitch is more preferably in the range of 25  $\mu\text{m}$  to 75  $\mu\text{m}$ . Furthermore, there is a tendency that the addition of a chiral agent decreases the drive voltage.

#### Example 5

Example 5 is the case where light transmittance and contrast can be improved in a liquid crystal display device in which liquid crystal domains are aligned in a radial manner or in a random manner. Hereinafter, Example 5 will be described by way of illustrating applications.

Applications 17, 18, 19 and 20

Two glass substrates with a thickness of 1.1 mm having ITO (a mixture of indium oxide and tin oxide with a thickness of 500 Angstroms) were used. Spacers with a diameter of 6  $\mu\text{m}$  were dispersed on one substrate, and the other substrate was placed thereon so as to keep a gap therebetween. Then, a photomask as shown in Figure 31 was placed on the cell thus obtained so that the pixels were covered with masking portions of the photomask. Moreover, in the cell, a homogeneous mixture containing 0.1 g of acrylate with two functional groups, i.e., a photopolymerizable compound (R-684, manufactured by Nippon Kayaku K.K.), 0.05 g of styrene, 0.85 g of isobornyl methacrylate, fluorine and/or chlorine type liquid crystal material shown in Table 10 (in which 0.5% of S-811 was added as a chiral agent), and 0.0025 g of a photopolymerization initiator (Irgacure 651) was injected.

Table 10

Liquid crystal materials used in Application 17 to 20				
	Application 17	Application 18	Application 19	Application 20
Anisotropy of refractive ratio of liquid crystal ( $\Delta n$ )	0.09	0.13	0.17	1.18
$d \cdot \Delta n$ ( $\mu\text{m}$ )	0.54	0.78	1.02	1.08

Next, the cell was irradiated with UV-rays through the photomask by using a high-pressure mercury lamp (which can provide parallel rays) at an illuminance of 10 mW/cm<sup>2</sup> under the condition that a cycle including one second irradiation and 30 seconds non-irradiation was repeated 20 times and then continuously irradiated for 10 minutes. Moreover, the cell was irradiated for 10 minutes without the photomask. Polarizing plates were attached to the upper and lower sides of the resulting cell so that each polarizing direction crossed the other at right angles. Thus, a liquid crystal display device in which liquid crystal regions were partitioned by polymer walls.

Table 11 shows light transmittance  $T_0$  which is an electro-optic characteristic of the cell thus formed under no applied voltage, where light transmittance obtained when the two polarizing plates are positioned so that each polarizing direction is aligned is taken as 100%.

Table 11

	Application 17	Application 18	Application 19	Application 20
Light transmittance $T_0$ (%)	33	36	31	29

Viewing angle characteristics of the liquid crystal display devices of Applications 17 to 20 were satisfactory without inversion phenomenon.

Applications 21 and 22

The same material for a substrate as that of Application 17 was used, and each cell was formed so as to have a cell thickness of 7.2  $\mu\text{m}$  (Application 21) and 9.1  $\mu\text{m}$  (Application 22) by changing the spacers to be provided in each cell.

The same mixture as that of Application 17 was injected into the respective cells, and the cells were irradiated with UV-rays through a photomask in the same way as in Application 17. The cells were observed by a polarizing microscope, which revealed the following:

In Applications 21 and 22, liquid crystal regions each having almost the same shape as that of a masking portion of the photomask were formed.

Comparative Examples 15 and 16

Cells were formed in the same way as in Applications 21 and 22, except that the thickness thereof is

changed. In Comparative Example 15, the cell thickness was 3.5  $\mu\text{m}$ , and in Comparative Example 16, the cell thickness was 12.0  $\mu\text{m}$ .

Table 12 shows the electro-optic characteristics of the liquid crystal display devices manufactured as described above.

Table 12

	Application 21	Application 22	Comparative Example 15	Comparative Example 16
Cell thickness ( $\mu\text{m}$ )	7.2	9.1	3.5	12.0
$d \cdot \Delta n$	0.648	0.819	0.315	1.17
Light transmittance $T_0$ (%)	38	32	12	20

As is understood from Table 12, the viewing angle characteristics of the liquid crystal display devices of Applications 21 and 22 were satisfactory without inversion phenomenon. Moreover, as is understood from Tables 10 to 12, display characteristics of the liquid crystal display devices, particularly, light transmittance  $T_0$  under no applied voltage are greatly influenced by a product of  $\Delta n$  of the liquid crystal material and the thickness  $d$  of the liquid crystal layer ( $\Delta n \cdot d$ ). In the case of the product  $\Delta n \cdot d$  of 0.4 to 1.1  $\mu\text{m}$ , higher light transmittance is obtained. In Comparative Example 15, since the cell thickness was too small, the liquid crystal material and the light-curable material do not sufficiently move; as a result, polymer walls were also formed in weak light-irradiated regions. Thus, light transmittance is low under no applied voltage. Moreover, the cell thickness influences the product  $\Delta n \cdot d$ . When the cell thickness was 3  $\mu\text{m}$  or less, the liquid crystal material and the light-curable material do not sufficiently move; as a result, a great number of liquid crystal regions are formed in the weak light-irradiated regions, decreasing contrast. When the cell thickness is 10 or more, part of the polymer walls is not sufficiently in contact with the upper and lower substrates, decreasing the controllability of the size of liquid crystal regions. Thus, it is preferred that the product  $\Delta n \cdot d$  is in the range of 0.4 to 1.1  $\mu\text{m}$ , and the cell thickness is in the range of 3 to 10  $\mu\text{m}$ .

#### Example 6

In the present example, a photomask preferred for manufacturing a liquid crystal display device in which liquid crystal domains are aligned in a radial manner or in a random manner.

A cell was formed in the same way as in Application 17. Then, the same mixture as that of Application 17 was injected into the cell. A photomask shown in Figure 32 was placed on the cell and irradiated with UV-rays in the same way as in Application 17. The observation of the cell thus obtained by a polarizing microscope revealed that liquid crystal regions as shown in Figure 33 were formed. Each liquid crystal region **d** had a structure in which an inside liquid crystal region **d1** and an outside liquid crystal region **d2** were separated by a polymer region, and a polymer island **i** was formed in the vicinity of the center of the inside liquid crystal region **d1**.

Figures 34A, 34B, and 34C show viewing angle characteristic curves of the liquid crystal display device obtained in the present example. Figures 34A and 34B show the relationships between the light transmittance and the applied voltage of the liquid crystal display device in which a cell was sandwiched by polarizing plates so that each polarizing direction crossed the other at right angles. As shown in Figure 34D, in Figure 34A, the viewing angle characteristic was measured in a direction **a** (i.e., in a vertical direction with respect to the cell); in Figure 34B, the viewing angle characteristic was measured in a direction **b** (i.e., in a direction with an angle of 40° from the vertical direction with respect to the cell); and in Figure 34C, the viewing angle characteristic was measured in a direction **c** (i.e., in a direction with an angle of 90° from the direction **b** and with an angle of 40° from the direction **a**). As is understood from those figures, even though the viewing angle is changed, the light transmittance and the applied voltage characteristic curves are hardly changed, showing that the viewing characteristic of the liquid crystal display device of the present example is excellent. In particular, it is hardly seen that the light transmittance is increased under an applied saturation voltage.

As in the present example, when a photomask, in which each masking portion has an opening whose shape is the same as that of a periphery of the masking portion, is used, small liquid crystal domains are formed in a radial manner between the periphery and the opening, thereby greatly improving the viewing angle charac-

teristic. The shape of the periphery and the opening is not necessarily identical. For example, a circular opening, a hexagonal opening, a square opening, etc. with respect to a rectangular periphery can provide the same advantages. In the case where the hexagonal shape is used as in the present example, a flat surface can entirely be covered, and the liquid crystal domains can readily be formed in a nearly circular liquid crystal region.

#### Example 7

Example 7 is the case where viewing angle dependency is further improved in a non light scattering type liquid crystal display device.

In a non light scattering type liquid crystal display device, a viewing angle characteristic in a half tone is much improved, compared with a conventional liquid crystal display device. However, liquid crystal molecules tilt with respect to a vertical direction of a cell, so that a refractive index of the vertical direction of the cell and that of a diagonal direction of the cell are slightly changed. Due to this phenomenon, apparent contrast is also slightly changed. In order to correct this phenomenon, a disk-shaped refractive index anisotropic film 62 having anisotropy of refractive index can be formed between a polarizing plate (not shown) and a substrate 61, as shown in Figure 18. Because of this, the refractive index in a vertical direction (m direction) and in a diagonal direction (n direction) become almost the same, thereby remarkably decreasing viewing angle dependency on contrast. This is disclosed in Japanese Laid-Open Patent Publication No. 2-400795. This is a general method for canceling birefringence.

The refractive index film 62 is formed of a biaxially oriented film such as polyvinyl alcohol (PVA), in which there is no anisotropy of refractive index in a film surface and the refractive index in a surface direction of the film is made larger than that in a vertical direction thereof.

#### Example 8

Example 8 is the case where a masking property is improved in a non light scattering type liquid crystal display device by placing a light-intercepting mask such as a black mask on a polymer wall.

Figure 19 is a cross-sectional view showing a liquid crystal display device according to the present example. This liquid crystal display device includes two transparent substrates 30 and 35 facing each other, polymer walls 37 provided so as to reach inner surfaces (strictly speaking, orientation films 34a and 34b) of the substrates 30 and 35, liquid crystal regions 38 partitioned by the polymer walls 37, polarizing plates 39a and 39b respectively provided on the outer surface of the substrates 30 and 35, and a backlight 40 provided outside of one (lower) substrate 30.

The substrate 30 has pixel electrodes 31 formed on the side of the liquid crystal regions 38. Moreover, on the substrate 30 having the pixel electrodes 31, a flat film 32 for flattening, a light-intercepting mask 33, and the orientation film 34a are formed in this order. The light-intercepting mask 33 is provided so that its masking portions cover 50% or more of each contact area where the polymer walls 37 are in contact with the inner surface of the substrate 30. The substrate 35 has counter electrodes 36 on the side of the liquid crystal regions 38 so that the counter electrodes 36 face and cross the pixel electrodes 31, and the orientation film 34b formed so as to cover the counter electrode 36.

When the masking portions of the light-intercepting mask 33 covers 100% or more of the contact area of the polymer walls 37, pixels correspond to portions which are not covered with the light-intercepting mask 33. In contrast, when the masking portions of the light-intercepting mask 33 covers less than 100% of the contact area of the polymer walls 37, pixels correspond to the area where the pixel electrodes 31 overlap the counter electrodes 36.

A liquid crystal display device with the above-mentioned structure is manufactured as follows:

First, the substrate 30 on which the pixel electrodes 31, the scanning lines, the signal lines, the flat film 32, the light-intercepting mask 33 and the orientation film 34a are formed, and the substrate 35 on which the counter electrode 36 and the orientation film 34b are obtained.

The orientation films 34a and 34b are subjected to a rubbing treatment. Then, the substrates 30 and 35 are disposed so as to face each other, and a previously prepared mixture at least containing a light-curable material and a liquid crystal material is injected between the substrates 30 and 35. Then, a photomask having masking portions is placed outside of the substrate 35. Each masking portion has a size smaller than that of each pixel, and the masking portions are formed in a matrix, the other portions of the photomask being light transmission portions. The position and size of the light transmission portions of the photomask are previously determined so that the masking portions of the light-intercepting mask 33 covers 50% or more of each area of the polymer walls 37 reaching the inner surface of the substrate 30.

As described above, it is preferred that the masking portions of the light-intercepting mask 33 cover 50%

or more of each area of the polymer walls 37 reaching the inner surface of the substrate 30. However, if 300% or more area is covered, the peripheral areas of the pixel electrodes 31 covered with the masking portions increase, resulting in a decrease in brightness. Thus, the percentage of each area of the polymer walls to be covered should be in the range of 50% to 300%. The range of 80% to 150% is more preferred. The use of the light-intercepting mask 33 has the following advantage:

Even though one liquid crystal region is provided over two pixels or one liquid crystal region is formed between the adjacent pixels, the light-intercepting mask 33 intercepts light between the adjacent pixels. Thus, light can be prevented from being transmitted between the adjacent pixels, thereby avoiding the decrease in contrast.

In the present example, the light-intercepting mask 33 is positioned on the side of the backlight 40 with respect to the liquid crystal regions 38. Alternatively, the light-intercepting mask can be positioned on the opposite side of the backlight 40 with respect to the liquid crystal regions 38. In the case where the light-intercepting mask 33 is positioned on the side of the backlight 40 with respect to the liquid crystal region 38, light can be intercepted before being scattered by the polymer walls 37. Thus, the light-intercepting property can be improved. In addition, the light-intercepting mask 33 is preferably provided close to the portions of the polymer walls 37 reaching the inner surface of the substrate 30 as much as possible.

Any material can be used for the light-intercepting mask 33 as long as visible light can be intercepted by 50% or more. Examples of the material include metal such as aluminum, tantalum, and molybdenum; or organic materials such as colored paints. The material is used as a thin film.

Hereinafter, Example 8 will be described by way of illustrating applications.

#### Application 23

First, electrode lines formed of ITO with a thickness of 500 Angstroms were respectively formed on PET films with a thickness of 0.25 mm. In both of the substrates, the width of each electrode line was 200  $\mu\text{m}$ ; the distance between the electrodes lines was 50  $\mu\text{m}$ ; and the respective number of the electrode lines was 20.

Next, polyimide (SE150, manufactured by Nissan Chemical Industries Ltd.) was coated onto the substrates by a spin coating method, whereby orientation films were formed. These orientation films were subjected to a rubbing treatment by using a nylon cloth. In this way, two substrates were formed.

Then, spacers with a diameter of 6  $\mu\text{m}$  were dispersed on one substrate, and the other substrate was placed thereon so as to keep a gap therebetween, whereby a cell was formed. At this time, the electrode lines formed on the respective PET films crossed each other at right angles.

A photomask 41 made of Al as shown in Figure 20 was placed on the cell thus obtained. The photomask 41 had square (for example) masking portions 41a, each side of which was 200  $\mu\text{m}$ . The distance between the respective centers of the adjacent square masking portions 41a was 250  $\mu\text{m}$ , and each width of light transmission portions 41b between the adjacent square masking portions 41a was 50  $\mu\text{m}$ . Then, a homogeneous mixture containing 0.1 g of trimethylol propane trimethacrylate, 0.9 g of 2-ethylhexyl acrylate, 4 g of a mixture in which 0.3 g of cholesteric nanonate (CN) was added to liquid crystal material (ZLI-3700-000, manufactured by Merck & Co., Inc.), and 0.03 g of a photopolymerization initiator (Irgacure 184, manufactured by CIBA-GEIGY Corporation) was injected into the cell.

The cell was irradiated with UV-rays by using a high-pressure mercury lamp which can provide parallel rays at an illuminance of 10 mW/cm<sup>2</sup> for two minutes.

Finally, polarizing plates were attached to the resulting cell so that the respective polarizing directions were aligned with the orientation directions of the corresponding orientation films, whereby a polymer dispersed TN liquid crystal display device was obtained.

#### Application 24

Another cell was formed as follows:

First, a cell was formed in the same way as in Application 23 except for the step of attaching the polarizing plates. Then, a light-intercepting mask 42 as shown in Figure 21 was attached to the cell. The light-intercepting mask 42 made of molybdenum had masking portions 42a (which just correspond to the light transmission portions of the photomask 41 in Application 23). The light-intercepting mask 42 was attached to the substrate which was to be on the side of a backlight so that the masking portions 42a overlapped the light transmission portions of the photomask 41.

Finally, polarizing plates were attached to the resulting cell so that the respective polarizing directions were aligned with the orientation directions of the corresponding orientation films, whereby a polymer dispersed TN liquid crystal display device was manufactured.

Comparative Example 17

As a comparative example with respect to Applications 23 and 24, a cell was formed in the same way as in Application 23 by using glass with ITO (flint glass with ITO having a thickness of 500 Angstroms, manufactured by Nippon Sheet Glass Co., Ltd.) instead of the substrate used in Application 23. Moreover, only the same liquid crystal as that of Application 23 was injected into the cell. Then, polarizing plates were attached to the cell so that the respective polarizing directions were aligned with the orientation directions of the corresponding orientation films, whereby a conventional TN liquid crystal display device was manufactured.

Comparative Example 18

As a comparative example with respect to Applications 23 and 24, a TN type cell was formed in the same way as in Application 23. Moreover, the same mixture as that of Application 23 was injected into the cell. Then, the cell was irradiated with UV-rays in the same way as Application 23, except that a photomask was not used, whereby a polymer dispersed liquid crystal display device was manufactured.

Table 13 shows contrast characteristics of the liquid crystal display devices of Applications 23 and 24 together with those of Comparative Examples 17 and 18.

Table 13

Comparison of contrast characteristics				
	Application 23	Application 24	Comparative Example 17	Comparative Example 18
Contrast	38	40	41	9

As is understood from Table 13, the liquid crystal display device of Application 23 has an electro-optic characteristic comparable to that of Comparative Example 17. In particular, the liquid crystal display device of Application 24 exhibits almost the same contrast as that of Comparative Example 17. Much more satisfactory contrast can be obtained in Applications 23 and 24, compared with that of Comparative Example 18.

Thus, according to the method of Example 8, a film-shaped substrate can be used, and higher contrast can be obtained, compared with the conventional polymer dispersed liquid crystal display device, because of little light scattering in the pixels.

The liquid crystal display devices of Applications 23 and 24 were cut and one substrate was peeled off from the other substrate in liquid nitrogen. Then, the liquid crystal material was washed away with acetone. After that, a horizontal cross-section of the polymer walls was observed by the SEM, revealing that the liquid crystal regions with the same regularity as that of the masking portions of the photomask (i.e., the same regularity as that of the pixels) were uniformly formed, each liquid crystal region having almost the same size.

In Example 8, each item described in Example 2, such as the Light regulating means such as a photomask, irradiation of light, etc. can be applied in the same way.

Example 9

Example 9 is the case where a photopolymerizable compound material and liquid crystal are clearly separated (phase separation) by curing the material in a non light scattering type liquid crystal display device.

In this type of liquid crystal display device, at least one substrate has an orientation film containing a thin film material and a photopolymerization initiator, and the substrate with the orientation film is subjected to a rubbing treatment in one direction.

A method for manufacturing this liquid crystal display device will be described as follows:

First, two substrates having the above-mentioned orientation films are disposed so that the respective orientation films face each other, whereby a cell is formed. Then, a mixture containing a liquid crystal material and a photopolymerizable material is injected between the substrates. When the cell thus formed is irradiated with light, the polymerizable material starts being polymerized due to the photopolymerization initiator contained in the orientation films. As a result, polymer walls are formed in desired positions.

Hereinafter, materials and the like applicable to the present example will be described.

(A thin film material for an orientation film)

In general, polymer materials, inorganic materials, and the like can be used. Organic materials such as polyimide, thermoplastic resins, and condensation type polymers are preferred. Examples of the polyimide include JALS-203 and JALS-204. (both manufactured by Nippon Chemical Industries Ltd.), and SE150 (manufactured by Japan Synthetic Rubber Co., Ltd.) etc. Examples of the thermoplastic resins include polystyrene, PMMA, polyphenylene oxide (PPO), polycarbonate, etc. Examples of the condensation type polymers include polyimide, novolac resins, etc.

(A photopolymerization initiator)

A general photopolymerization initiator can be used. Examples of the photopolymerization initiator include Irgacure 184, Irgacure 651, Irgacure 907, Darocure 1173, Darocure 1116, and Darocure 2959, etc. The photopolymerization initiator can be added in the range of 1 to 50% by weight based on the total weight of the above-mentioned thin film material.

The thin film material and the photopolymerization initiator are dissolved in a solvent (which allows the thin film material and the photopolymerization initiator to be dissolved) to obtain a dilute solution. The solution thus obtained is coated onto the substrate by a spin coating method, a printing method, etc., whereby an orientation film is formed.

Hereinafter, Example 9 will be described by way of illustrating applications.

#### Application 25

Figure 35 is a schematic cross-sectional view of a polymer dispersed liquid crystal display device of the present example. Figure 36 is a cross-sectional view showing one step of a method for manufacturing the polymer dispersed liquid crystal display device. As shown in Figure 35, a pair of substrates 71 and 72 face each other so as to have liquid crystal regions 78 supported by polymer walls 77. Electrode lines 73 are provided on an inner side of the substrate 71, and an orientation film 75 is formed so as to cover the electrode lines 73. Electrode lines 74 are provided on an inner side of the substrate 72, and an orientation film 76 is formed so as to cover the electrode lines 74.

The liquid crystal display device with the above-mentioned structure was manufactured as follows:

As shown in Figure 36, the electrode lines 73 and 74 formed of ITO (a mixture of indium oxide and tin oxide) were formed on the substrates 71 and 72, respectively. The thickness of the respective substrates 71 and 72 was 1.1 mm. Each thickness and width of the electrode lines 73 and 74 was 500 Angstroms and 200  $\mu\text{m}$ . Twenty electrode lines 73 and 74 were respectively formed with a distance of 50  $\mu\text{m}$  between adjacent lines. Glass with ITO (flint glass with ITO having a thickness of 500 Angstroms, manufactured by Nippon Sheet Glass Co., Ltd.) can be used for the substrates 71 and 72.

Then, the orientation films 75 and 76 were coated so as to cover the electrode lines 73 and 74, respectively by a spin coating method. The orientation films 75 and 76 were subjected to a rubbing treatment in one direction by using a nylon cloth. The orientation films 75 and 76 were formed of polyimide (SE150, manufactured by Nissan Chemical Industries Ltd.) to which 5% by weight of a photopolymerization initiator (Irgacure 184) was added. The substrates 71 and 72 thus obtained were attached so that the electrode lines 73 and 74 faced and crossed each other. Then, spacers with a diameter of 6  $\mu\text{m}$  were dispersed on one of the substrates 71 and 72, and the other substrate was placed thereon, whereby a cell was formed.

Next, a photomask 79 was placed outside of the substrate 72 so that pixel portions were masked. Moreover, a homogeneous mixture 80 containing a photopolymerizable material and a liquid crystal material was injected into the cell. The photopolymerizable material contained 0.1 g of trimethylol propane trimethacrylate, 0.4 g of 2-ethylhexyl acrylate, and 0.5 g of isobornyl acrylate; and the liquid crystal material contained 4 g of a mixture in which 0.3% of cholesteric nanonate (CN) was added to ZLI-3700-000 (manufactured by Merck & Co., Inc.). The cell thus obtained was irradiated with UV-rays at an illuminance of 10 mW/cm<sup>2</sup> for 10 minutes by using a high-pressure mercury lamp which can provide parallel rays, whereby the photopolymerizable material was cured.

One substrate was peeled off from the other substrate in liquid nitrogen, and the liquid crystal material was washed away with acetone. After that, a horizontal cross-section of the polymer walls was observed by the SEM, revealing that liquid crystal regions 78 with the same regularity as that of the photomask 79 (i.e., the same regularity as that of the pixels) were uniformly formed, each liquid crystal region 78 having almost the same size. Here, it is noted that 20 polymer walls which had the most excellent regularity were selected for observation from samples, since some of the samples were damaged during the formation thereof.

Finally, two polarizing plates were attached to the cell so that each polarizing direction was aligned with the orientation direction of the cell, whereby a liquid crystal display device of the present example was manufactured.

#### Comparative Example 19

As a comparative example with respect to Application 25, a liquid crystal display device was manufactured as follows:

In Comparative Example 19, glass with ITO (flint glass with ITO having a thickness of 500 Angstroms, manufactured by Nippon Sheet Glass Co., Ltd.) was used instead of the substrates 71 and 72 of application 25, and only a liquid crystal material (ZLI-3700-000) was used.

#### Comparative Example 20

As a comparative example with respect to Application 25, and a liquid crystal display device was manufactured in the same way as in Application 25 except that a photomask was not used.

Table 14 shows the results obtained by measuring the contrast of the liquid crystal display devices of Application 25 and Comparative Examples 19 and 20. Contrast is measured by using a Photol LC 5000 system, and is taken as a ratio of light transmittance  $T_0$  under no applied voltage with respect to light transmittance  $T_{sat}$  under the condition that a saturation voltage is applied: ( $T_0/T_{sat}$ ).

Table 14

Comparison of contrast characteristics			
	Application 25	Comparative Example 19	Comparative Example 20
Contrast	39	41	9

As is understood from Table 14, the liquid crystal display device manufactured by using a photomask has high contrast. The use of the photomask enables the formation of the polymer walls with the same regularity as that of the pixels and greatly decreases the interfaces between the polymer walls and the liquid crystal regions, sufficiently reducing light scattering between the polymer walls and the liquid crystal regions.

In Example 9, each item described in Example 2, such as Light regulating means such as a photomask, irradiation of light, etc. can be applied in the same way.

#### Example 10

Example 10 is the case where a phase separation is clearly conducted between a polymer and liquid crystal by curing a photopolymerizable compound in a non light scattering type polymer dispersed liquid crystal display device.

Figure 37 shows a cross-sectional view illustrating a method for manufacturing a polymer dispersed liquid crystal display device of the present example. Figure 38 shows a schematic cross-sectional view of the polymer dispersed liquid crystal display device of the present example. As shown in Figure 37, substrates 81 and 82 face each other with liquid crystal regions 88 sandwiched therebetween. The liquid crystal regions 88 are partitioned by polymer walls 87. The substrate 81 has electrode lines 83 on the side of the liquid crystal regions 88, and an orientation film 85 is formed so as to cover the electrode lines 83. On the orientation film 85 other than pixels 92, a thin film pattern 89 containing a polymerization initiator are formed. Electrode lines 84 are provided on an inner side of the substrate 82, and an orientation film 86 is formed so as to cover the electrode lines 84. On the orientation film 86 other than the pixels 92, a thin film pattern 90 containing a polymerization initiator is formed.

A method for manufacturing the liquid crystal display device with the above-mentioned structure is as follows:

First, the thin film patterns 89 and 90 containing a polymerization initiator are respectively formed on portions of the substrates 81 and 82 in which the polymer walls 87 are to be formed. Then, the substrates 81 and 82 are attached to each other, and a mixture containing a liquid crystal material and photopolymerizable or heat-polymerizable compound material is injected between the substrates 81 and 82 whereby a cell is formed. Next, the mixture is irradiated with UV-rays or heated. As a result, the polymerizable compound starts being



cured due to the polymerization initiator contained in the thin film patterns 89 and 90, and the polymer walls 87 starts being formed in contact with the thin film patterns 89 and 90. Thus, the liquid crystal regions 88 which are subjected to orientation treatment are formed in one pixel or an adjacent plurality of pixels.

The thin film pattern is prepared by adding a polymerization initiator to a supporter and then dissolving the mixture in a solvent, thereby obtaining a dilute solution. The thin film pattern is formed at least one substrate so as to cover the electrode lines formed on the substrate. Preferably, the same thin film patterns are formed on both substrates.

Hereinafter, materials and a method for manufacturing applicable to the present example will be described.

#### (A thin film pattern)

It is preferred that a thin film pattern does not cover 60% or more of each area of the pixels. When the thin film pattern covers 60% or more of each area of the pixels, polymer walls formed in the pixel portions which are covered with the thin film pattern cause light scattering, decreasing contrast.

The shape of a portion on which the thin film pattern is not formed (i.e., the shape of a portion in which a liquid crystal region is formed) is not particularly limited. Preferred shapes include a circle, a square, a trapezoid, a hexagon, a rectangle, a diamond shape, a letter shape, a shape surrounded by a curved line(s) and/or a straight line(s), a configuration obtained by cutting a part of these shapes, a configuration obtained by the combination of the different shapes, a configuration obtained by the combination of the same shapes, and the like. When the present invention is put into practical use, one or more of these shapes is selected. In order to improve productivity of the liquid crystal region, it is preferred to limit the configuration to one shape with the same size.

Moreover, as shown in Figure 39, as in the present example, it is preferred to form the thin film pattern on the entire portions other than pixels. Because this structure decreases the intensity of light scattering in the pixels and improves the contrast of the liquid crystal display device. Alternatively, the thin film pattern can be formed on a part of the portions other than pixels. For example, as shown in Figure 40, the thin film pattern is formed in a line shape or as shown in Figure 41, the above-mentioned shapes are combined as one pixel.

#### (A method for forming a thin film pattern)

An example of the method for forming a thin film pattern includes a printing method or lithography used in the semiconductor industry.

In the printing method, a material obtained by adding a polymerization initiator to a supporter and dissolving the mixture in a solvent is formed into a thin film pattern by a seal printing, a screen printing, an offset printing, etc. As the supporter, a polymer material can be used. Examples of the polymer material include methyl polymethacrylate (PMMA), polyvinyl alcohol, nitrocellulose, polycarbonate, vinyl acetate, polyimide, etc. The solvent depends upon the material of the supporter to be used. The examples of the solvent include toluene, methyl ethyl ketone (MEK),  $\gamma$ -butyrolactone, etc. The mixture of the supporter and the polymerization initiator is dissolved in the solvent to obtain a solution containing the mixture in an amount of 0.1 to 50% by weight.

In the photolithography, a polymerization initiator is added to a positive resist material, and the mixture is coated onto at least one of the two substrates. Then, a photomask is placed on the substrate, on which the mixture is coated, so that a thin film pattern is formed on a desired place, and under this condition, the substrate is exposed to light. After that, a resist material on a light-exposed portion is removed. An example of the positive resist material includes AZ1350 (manufactured by Shipley Corporation).

#### (A polymerization initiator)

As a polymerization initiator, a photopolymerization initiator and a thermal polymerization initiator can be used. Examples of the photopolymerization initiator include Irgacure 184, Irgacure 651, Irgacure 907, Darocure 1173, Darocure 1116, and Darocure 2959. Examples of the thermal polymerization initiator include peroxides such as BPO and t-butylperoxide; radical generating agents such as azobisisobutyronitrile (AIBN); and amine compounds such as ethylamine, n-butylamine, benzylamine, diethylenetriamine, tetramethylenepentamine, diaminodiphenylmethane.

#### (A thickness of a cell)

When two substrates face each other, the thickness of a cell is varied depending upon a display mode. In the case of photostetting, the thickness of the cell is preferably larger than a dot diameter of the photomask

to be used. Due to this, liquid crystal regions are formed in a column-shaped honeycomb structure, decreasing the intensity of light scattering in pixels and improving the contrast of the liquid crystal display device.

5 (A polymerizable compound material)

In addition to the materials described in "A polymerizable material" of Example 2, a thermosetting monomer can be used as the polymerizable compound material. Examples of the thermosetting monomer include bisphenol A type epoxy resins, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, hexahydrobisphenol A diglycidyl ether, propylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, diglycidylester phthalate, triglycidyl isocyanate, tetraglycidylmethaxylenediamine, etc. These monomers can be used alone or in combinations of two or more kinds. As the light-curable and thermosetting oligomers and polymers, for example, chlorinated and/or fluorinated polymers obtained from these monomers can be used. These monomers, oligomers, and polymers can be used in combination.

15 (A method for curing a polymerizable compound material)

A polymerizable compound material is cured by being irradiated with light or by being heated.

In the case of the light irradiation, it is preferred that the UV-rays to be used are parallel rays. Here, when ferroelectric liquid crystal (FLC) is used, it is effective for improving shock resistance to provide small liquid crystal droplets as a buffer at the periphery of large liquid crystal regions with almost the same size as that of pixels. Thus, for the purpose of forming such small liquid crystal droplets, the end portions of the photomask are made so that much more light can be transmitted toward outside of the photomask; the photomask is placed away from the substrate; and UV-rays with a relatively poor degree of parallelization are used. It is preferred to select the polymerizable compound material and the liquid crystal material so that the diameter of each liquid crystal region becomes larger than a dot diameter of the photomask used during the UV-rays irradiation step. However, even though the selected polymerizable compound material and liquid crystal material make the diameter of each liquid crystal region smaller than a dot diameter of the photomask, these selected materials can be used by decreasing the intensity of UV-rays, conducting the reaction at low temperatures over a long period of time, and reducing the added amount of the polymerization initiator.

Moreover, the shape of the photomask to be used is not particularly limited as long as it appropriately decreases the intensity of UV-rays. It is preferred that the photomask is provided so that each masking portion thereof covers 30% or more of the size of each pixel and 50% or more of each portion of a thin film pattern is exposed to light. When each masking portion of the photomask covers less than 30% of the size of each pixel, each liquid crystal region obtained has a size corresponding to less than 30% of the size of each pixel. As a result, the number of interfaces between the liquid crystal regions and the polymer walls are formed in pixels, increasing the degree of light scattering in the pixels and decreasing contrast. Therefore, this case is not preferred. When less than 50% of each portion of the thin film pattern is exposed to light, the area occupied by the liquid crystal regions formed is reduced, resulting in the decrease in overall contrast. Thus, this case is not preferred, either.

In the case of thermosetting, when the reaction rate is low, polymer walls are formed in liquid crystal regions due to the formation of polymerized ends in the liquid crystal regions, decreasing contrast. Thus, it is preferred to select a reaction system and reaction conditions which allow reaction to be completed within 10 minutes.

45 Hereinafter, Example 10 will be described by way of illustrating Applications.

## Application 26

A liquid crystal display device with a structure shown in Figure 37 was manufactured by the following method:

First, as shown in Figure 37, the electrodes 83 and 84 formed of ITO (a mixture of indium oxide and tin oxide) were formed on the substrates 81 and 82. As the substrates 81 and 82, flint glass (manufactured by Nippon Sheet Glass Co., Ltd.) with a thickness of 1.1 mm, a length of 30 mm, and a width of 30 mm was used. The electrode lines 83 and 84 had a thickness of 500 Angstroms and a width of 200  $\mu\text{m}$ . The respective electrode lines 83 and 84 were formed with a distance between them of 50  $\mu\text{m}$ . The respective number of the electrode lines 83 and 84 was 100. Then, polyimide (SE150, manufactured by Nissan Chemical Industries Ltd.) was respectively coated so as to cover the electrode lines 83 and 84 by a spin coating method. The polyimide was cured by heating to form orientation films 85 and 86. The orientation films 85 and 86 were subjected to a rubbing treatment in one direction with a nylon cloth.

Next, the thin film patterns **89** and **90** were formed on the orientation films **85** and **86**, respectively by the following method:

First, a solution in which a photopolymerization initiator (Irgacure 184) was added to a positive resist material (i.e., a supporter) (AZ1350, manufactured by Shipley Corporation) in an amount of 5% by weight was coated onto the orientation films **85** and **86** by a spin coating method, thereby forming positive photoresists. Then, a photomask was placed on each photoresist so that its masking portions covered portions of the positive photoresist other than the portions to be pixels **92**. Under this condition, UV-rays were irradiated to each photoresist at an illuminance of 15 mW/cm<sup>2</sup> (measured at 365 nm) by using a high-pressure mercury lamp and developed with a developer. Then, photoresist portions exposed to light were removed to obtain the thin film patterns **89** and **90** as shown in Figure 38. Here, the portions of the photoresist patterns **89** and **90** other than the portions to be pixels **92** correspond to portions between the adjacent electrode lines **83** formed on the substrate **81** and portions between the adjacent electrode lines **84** formed on the substrate **82**.

Spacers with a diameter of 6  $\mu$ m were dispersed on one of the substrates **81** and **82** and the other substrate was placed thereon so as to keep a gap therebetween, whereby a cell was formed. At this time, the electrode lines **83** and **84** faced and crossed each other.

Next, as shown in Figure 38, a photomask **91** was placed on the substrate **82** so that its masking portions covered the pixels **92**. Moreover, a homogeneous mixture **93** containing a photopolymerizable compound material and a liquid crystal material was injected into the cell. Then, the cell was irradiated with UV-rays at an illuminance of 10 mW/cm<sup>2</sup> for 5 minutes by using a high-pressure mercury lamp which can provide parallel rays, whereby the photopolymerizable compound material was cured. As the photopolymerizable compound material, a mixture containing 0.1 g of trimethylol propane methacrylate, 0.4 g of 2-ethylhexyl acrylate, and 0.5 g of isobornyl acrylate was used. As the liquid crystal material, 4 g of a mixture in which 0.3% of cholesteric nano-nate was added to ZLI-3700-000 (manufactured by Merck & Co., Inc.) was used. As a result, as shown in Figure 37, in regions which were irradiated with the UV-rays, polymer walls **87** with high physical strength were formed in contact with the thin film patterns **89** and **90**; and in regions which were covered with the masking portions of the photomask **91**, the liquid crystal regions **88** subjected to orientation treatment were formed in contact with the orientation films **85** and **86**.

The cell thus obtained was sandwiched by two polarizing plates so that the respective polarizing directions were aligned with the orientation directions of the corresponding orientation films, whereby a liquid crystal display device of Application 26 was obtained.

One substrate was peeled off from the other substrate in liquid nitrogen, and the liquid crystal material was washed away with acetone. After that, a horizontal cross-section of the polymer walls was observed by the SEM, revealing that liquid crystal regions with the same regularity as that of a pattern of the photomask **91** (i.e., the same distribution as that of the pixels **92**) were uniformly formed, each liquid crystal region having almost the same size. The polymer walls were likely to be damaged while forming samples, so that 20 polymer walls which had the most excellent regularity among the samples were selected for observation.

#### Application 27

First, the electrode lines **83** and **84**, and the orientation films **85** and **86** were formed on the substrates **81** and **82** in the same way as in Application 26. Then, the rubbing treatment was conducted in the same way as in Application 26.

Next, the same photopolymerization initiator as that of Application 26 was added in an amount of 5% by weight to a supporter (polystyrene), and the mixture was diluted with toluene to obtain 3% by weight of solution. Then, on portions of the orientation films **85** and **86** other than portions to be pixels **92**, the toluene solution thus obtained was printed by seal printing to form thin film patterns **89** and **90**, respectively with a thickness of 1  $\mu$ m after being dried. The thin film patterns **89** and **90** had the same pattern. Then, a cell was formed in the same way as in Application 26, the photomask **91** was mounted, and the same mixture **93** as that of Application 26 was injected into the cell. After that, the cell was irradiated with UV-rays in the same way as in Application 26, whereby the photopolymerizable compound material was cured. The cell was sandwiched by two polarizing plates in the same way as in Application 26, whereby a liquid crystal display device of Application 27 was obtained.

#### Comparative Example 21

A conventional TN liquid crystal display device (which is not a polymer dispersed type) was manufactured.

### Comparative Example 22

A liquid crystal display device was manufactured in the same way as in Application 26, except that the thin film patterns **89** and **90** were not formed.

Table 15 shows the results obtained by measuring the contrast of the liquid crystal display devices of Applications 26 and 27, and those of Comparative Examples 21 and 22. The contrast is taken as a ratio of transmittance of light passing through a liquid crystal display device under no voltage with respect to light transmittance under the condition that a voltage of 10 V is applied to electrodes, i.e., (light transmittance under no applied voltage)/(light transmittance under the condition of a voltage 10V applied).

Table 15

Comparison of contrast characteristics				
	Application 26	Application 27	Comparative Example 21	Comparative Example 22
Contrast	39	37	41	9

As is understood from Table 15, the polymer dispersed liquid crystal display devices of Applications 26 and 27 in which the thin film patterns **89** and **90** are formed have high contrast. The liquid crystal display device of Comparative Example 21 which is not a polymer dispersed type also has high contrast. However, when this device was raised, a rough display was observed on the upper and lower parts. It is understood from this result that the formation of the thin film patterns **89** and **90** enables a clear separation between the liquid crystal regions and the polymer walls, greatly decreases interfaces between the liquid crystal regions and the polymer walls in the pixels **92**, and sufficiently reduces the light scattering between the liquid crystal regions and the polymer walls.

Items described in Example 2: A light regulating means such as a photomask, Irradiation light, etc. can be applied to Example 10.

### Example 11

Example 11 is the case where the response speed is sufficiently improved and a high electrical holding ratio can be maintained. The present example will be described by way of illustrating Applications.

### Application 28

Figure 42 is a cross-sectional view showing a liquid crystal display device of Application 28. In the liquid crystal display device, a display medium is provided between two facing substrates **101** and **102**. The display medium has a structure in which liquid crystal regions **108** are partitioned by polymer walls **107** formed in a matrix. A plurality of electrode lines **103** are provided in parallel on a base substrate **101a**. Moreover, an orientation film **105** is formed so as to cover the electrode lines **103**. On the substrate **102**, a plurality of electrode lines **104** are provided in parallel on a substrate **102a**. Moreover, an orientation film **106** is formed so as to cover the electrode lines **104**. The electrode lines **104** are formed on the substrate **102** so as to cross the electrode lines **103** formed on the substrate **101** at right angles.

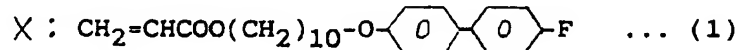
Each crossed portion of the electrode lines **103** and **104** defines a pixel **110** as shown in Figure 43. It is not necessary that the electrode lines **103** and **104** cross each other at right angles, and they may just cross each other. Furthermore, in the case where a display device is used in an active matrix system, e.g., a TFT is used as an active element formed on a pixel electrode on one substrate (generally, one TFT is provided for one pixel), one counter electrode can be used on the other substrate.

The display medium containing polymer walls **107** and liquid crystal regions **108** is obtained as follows:

A liquid crystal material and a polymerizable compound material containing a liquid crystalline compound having at least one polymerizable functional group in its molecule is mixed, and the mixture is polymerized. Thus, the display medium is obtained by a phase separation involved in this reaction. Each liquid crystal region **108** has a structure in which a polymerizable liquid crystalline compound **109** is present in the vicinity of the interface between the liquid crystal region **108** and the polymer wall **107**.

Hereinafter, a method for manufacturing a liquid crystal display device with the above-mentioned structure will be described.

First, a liquid crystalline compound having a polymerizable functional group in its molecule was prepared. The polymerizable liquid crystalline compound was referred to as, for example, a compound X (represented by the following Formula (1)).



The compound X was prepared as follows:

First, 4'-hydroxy-4-phlorobiphenyl was esterified by using excess 1,10-dibromodecane in the presence of calcium carbonate. Then, the esterified 4'-hydroxy-4-fluorobiphenyl was purified by a column chromatography, and the purified substance was mixed with an equimolar tetramethyleammonium-hydroxypentahydrate. The mixture thus obtained was esterified with acrylic acid to obtain a polymerizable liquid crystalline compound. The polymerizable liquid crystalline compound can previously be prepared.

Next, a pair of substrates each having electrode lines 103 and 104 on a PET film with a thickness of 0.25 mm were obtained. The electrode lines 103 and 104 were formed of ITO (a mixture of indium oxide and tin oxide), had a thickness of 500 Angstroms, a width of 200  $\mu\text{m}$ , and each electrode line was disposed with an interval of 50  $\mu\text{m}$  between lines. The number of the electrode lines 103 and that of the electrode lines 104 were 20, respectively. Polyimide obtained by adding 5% of a polymerization initiator (Irgacure184) to SE150 (manufactured by Nissan Chemical Industries Ltd.) was coated onto one substrate by a spin coating method. The coated film was subjected to a rubbing treatment by using a nylon cloth.

Spacers with a diameter of 6  $\mu\text{m}$  were dispersed on one of the substrates 101 and 102 and the other substrate was placed thereon so as to keep a predetermined gap therebetween, whereby a cell was formed. At this time, the electrode lines 103 and 104 crossed each other at right angles.

Then, a photomask having masking portions 111 for each pixel 110 as shown by shaded portions of Figure 43 (i.e., having masking portions in a dot pattern) was placed on the cell thus formed so that the masking portions 111 covered the pixels 110. Moreover, a homogeneous mixture previously prepared was injected into the cell. The mixture contained 0.1 g of trimethylol propane trimethacrylate, 0.35 g of 2-ethylhexyl acrylate, 0.45 g of isobornyl acrylate, 4 g of the compound X and a liquid crystal material (i.e., 0.2 g of the compound X and 3.8 g of a liquid crystal material (ZLI-4792, manufactured by Merck & Co., Inc.)) to which 0.3% of cholesteric nanonate (CN) was added, and 0.15 g of a polymerization initiator (Irgacure 184). Namely, the mixture contained a polymerizable material, a polymerizable liquid crystalline compound (compound X), a liquid crystal material, and a polymerization initiator. Then, the cell was irradiated through the photomask with UV-rays at an illuminance of 10 mW/cm<sup>2</sup> for 5 minutes by using a high-pressure mercury lamp which can provide parallel rays, whereby the polymerizable material was cured.

Another cell was separately formed in the same manner as the above, and one substrate of the cell was peeled off from the other substrate in liquid nitrogen, and the liquid crystal material was washed away with acetone. After that, a horizontal cross-section of the polymer walls was observed by an SEM, revealing that liquid crystal regions with the same regularity as that of a dot pattern of the photomask (i.e., the same regularity as that of the pixels 110) were uniformly formed, each liquid crystal droplet having almost the same size. Since the polymer walls 107 were likely to be damaged while forming a sample, 20 liquid crystal regions which had the most excellent regularity in the sample were selected for observation. Thus, the same regularity is required for the photomask.

Polarizing plates were attached to the cell so that the respective polarizing directions were aligned with the orientation directions of the corresponding orientation films, whereby a polymer dispersed liquid crystal display device of a TN mode was manufactured.

#### Comparative Example 23

As a comparative example with respect to Application 28, a liquid crystal display device was manufactured as follows:

A cell was formed in the same way as in Application 28, except that glass with ITO (flint glass with ITO having a thickness of 500 Angstroms, manufactured by Nippon Sheet Glass Co., Ltd.) was used instead of the substrates used in Application 28. Moreover, only the same liquid crystal material as that of Application 28 was injected into the cell. Then, polarizing plates were attached to the cell so that the respective polarizing directions were aligned with the orientation directions of the corresponding orientation films, whereby a conventional TN liquid crystal display device was manufactured.

### Comparative Example 24

As a comparative example with respect to Application 28, a TN cell was formed in the same way as in Application 28. Then, the same mixture as that of Application 28 containing the liquid crystal material and the light-curable material (to which the compound X was not added) was injected into the cell. The cell was irradiated with UV-rays in the same way as in Application 28 without a photomask, whereby a polymer dispersed liquid crystal display device was manufactured.

Table 16 shows the electro-optic characteristics of the liquid crystal display device of Application 28 together with those of the liquid crystal display devices of Comparative Examples 23 and 24.

Table 16

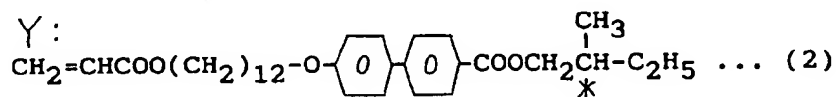
Comparison of electro-optic characteristics			
	Application 28	Comparative Example 23	Comparative Example 24
Contrast	40	41	9
Response speed $\tau_r + \tau_d$ (ms)	30	45	150

As is understood from Table 16, the liquid crystal display device of Application 28 has an electro-optic characteristic comparable to that of the liquid crystal display device of Comparative Example 23 which has conventionally been used. Moreover, in Application 28, the liquid crystal display device has less light scattering in pixels, compared with the conventional polymer dispersed liquid crystal display device (Comparative Example 24), so that contrast of the liquid crystal display device in Application 28 is remarkably high. Moreover, the response speed of Application 28 is about 5 times that of Comparative Example 24. Furthermore, the response speed of Application 28 is faster than that of the TN liquid crystal display device of Comparative Example 23 due to the effects of the liquid crystalline compound fixed on the polymer walls. In the present invention, the response speed was taken as a sum of a response speed ( $\tau_r$ ) under the condition that a saturation voltage was applied and a response speed ( $\tau_d$ ) under the condition that the saturation voltage was not applied.

In application 28, in order to use ZLI-4792 having fluorine as a liquid crystal material, a fluorine atom was contained in the polymerizable liquid crystalline compound as shown in Formula (1). Because of this, the liquid crystal molecules present in the vicinity of the interfaces between the liquid crystal regions and the polymer walls are chemically stabilized; as a result, a TFT of a charge holding type can be applied to the liquid crystal display device without decreasing the electrical holding ratio of an entire liquid crystal display device. Such advantages can also be obtained in the case where chlorine atoms are contained in the polymerizable liquid crystalline compound.

### Application 29

A liquid crystal display device was manufactured by changing the kinds of polymerizable liquid crystalline compound to be used. In Application 29, a polymerizable liquid crystalline compound prepared by using a ferroelectric compound Y represented by the following Formula (2) in accordance with "Liquid Crystal" vol. 9, No. 5, pp. 635-641 (1991) was used.



First, two substrates which were subjected to uniaxial orientation treatment in the same way as in Application 28 were made to face each other with silica beads having a diameter of 2  $\mu\text{m}$  sandwiched therebetween. At this time, each rubbing direction of the substrates was aligned. Then, a homogeneous mixture containing 0.018 g of trimethylol propane methacrylate, 0.060 g of lauryl acrylate, 0.020 g of compound Y, 0.002 g of a polymerization initiator (Irgacure 651), and 0.400 g of a ferroelectric liquid crystal material (ZLI-4237-000) was injected into the cell. Namely, the mixture contained the polymerizable material, the polymerizable liquid crystalline compound (compound Y), the polymerization initiator, and the ferroelectric liquid crystal material.

After that, a photomask was placed on the cell in the same way as in Application 28, and the cell was

irradiated through the photomask with UV-rays at 10 mW/cm<sup>2</sup> for 20 minutes by using a high-pressure mercury lamp which can provide parallel rays, whereby the polymerizable material was cured.

5     Comparative Example 25

          A mixture containing the ferroelectric liquid crystal (ZLI-4003) which was the same kind as that of Application 29 and a light-curable material excluding the compound Y was injected into the cell. Then, the cell was irradiated with UV-rays without a photomask in the same way as in Application 28, whereby a polymer dispersed liquid crystal display device was manufactured.

10     Comparative Example 26

          Only the ferroelectric liquid crystal (ZLI-4003) was injected between the substrates prepared in the same way as in Application 29, whereby a liquid crystal cell was formed.

15     Table 17 shows electro-optic characteristics of the cell of Application 29 and results obtained by measuring shock resistance together with those of the cells of Comparative Examples 25 and 26. The electro-optic characteristics were obtained by measuring a response speed, a memory pulse width, contrast, and applied pressure; and the shock resistance was measured by an impact test.

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Table 17

	Application 29	Comparative Example 25	Comparative Example 26
Response speed	130 $\mu$ sec	120 $\mu$ sec	150 $\mu$ sec
Memory pulse width	200 $\mu$ sec	180 $\mu$ sec	-
Contrast	35	40	5 or less
Pressure application test	10 kgf/cm <sup>2</sup>	1 kgf/cm <sup>2</sup>	10 kgf/cm <sup>2</sup>
Impact test	○	X	△

Note: In Comparative Example 26, the liquid crystal layer takes a certain state by the application of a voltage; however, it cannot hold the state, when a voltage is made 0 V. The liquid crystal molecules in the device are not in a symmetrical orientation which enables bistability.

The above-mentioned electro-optic characteristics were measured under the following conditions:

A cell was placed between polarizing plates of an optical characteristic measurement system under crossed Nicols. Then, the electro-optic characteristics of the cell were measured under the condition that the polarizing plate was rotated by 22.5° so that polarity of the electrical field and that of the signal from a photodetector coincided with each other (here, the angle of the polarizing plate, in which the maximum values of the photodetector with respect to the intensity of transmitted light in positive and negative electrical fields became almost the same, was taken as 0, when a rectangular wave with 100 Hz and  $\pm 10$  V was applied). Each measurement value was obtained as follows:



(Response speed)

A response speed is taken as the average time which is required for the optical amount of the cell to change from 10% to 90% when a pulse rises/falls as a result of the application of a rectangular wave with 100 Hz and  $\pm 10$  V.

(A memory pulse width)

A memory refers to a pulse width required for holding bistable two states, when a voltage is made 0 V. The two states are obtained, when voltages with different polarity are applied to the polymer dispersed liquid crystal layer (i.e., energy required for changing the two states expressed by the formula: Voltage x Pulse width (sec.) is given to the layer). In this case, a memory pulse width is a pulse width of a bipolar pulse of  $\pm 10$  V.

(Contrast)

Contrast is measured as  $(V_{ON} - V_D)/(V_{OFF} - V_D)$ , where  $V_{ON}$  is a photodetector signal in an ON state,  $V_{OFF}$  is a photodetector signal in an OFF state, and  $V_D$  is a photodetector signal in a dark state under the condition that a memory state of all of the pixels is switched.

(A pressure application test)

A pressure application test is conducted by a compression test using a pressure test machine (AGS-100A, manufactured by Shimadzu Seisakusho Ltd.). A cell is placed on a horizontal table, and a load is applied to the cell through a bar which is in contact with the cell in a horizontal manner. The diameter and the cross section of the bar are 8 mm and 0.670 cm<sup>2</sup>, respectively. The change of load is checked when the orientation is changed.

(An impact test)

The change of the orientation of the liquid crystal molecules in a cell is checked, when the cell is dropped from a height of 50 cm to a linoleum table. In Table 17, a mark ○ shows that the orientation is slightly disturbed between the polymer walls and the liquid crystal; however, no problem is caused for practical use. A mark × shows that the orientation is disturbed in the pixels. This indicates a problem for practical use. A mark Δ shows that the orientation state is partially disturbed due to the impact.

As is understood from Table 17, the cell of Application 29 is more excellent in the pressure application test and the impact test, compared with the cell of Comparative Example 25 using the same ferroelectric liquid crystal as that of Application 29. Moreover, in Comparative Example 26, the liquid crystal molecules are not sufficiently aligned, so that contrast is low. Furthermore, the cell of Comparative Example 26 cannot be measured in the impact test, since the orientation of the liquid crystal molecules are not sufficient from the beginning. In contrast, the cell of Application 29 provides satisfactory results in both of these tests.

As described above, according to Application 29, a mixture containing a liquid crystal material and a polymerizable compound material which contains a liquid crystalline compound having at least one polymerizable functional group in its molecule is polymerized. As a result of this reaction, a phase separation occurs between polymer walls and liquid crystal regions, whereby a display medium in which the liquid crystal regions are partitioned by the polymer walls is formed. On each interface between the polymer wall and the liquid crystal region, the liquid crystalline compound is fixed. Due to this structure, each interface between the liquid crystal region and the polymer wall is driven by the application of a voltage, and a driving force is increased under no applied voltage, since the liquid crystalline compound is bound to the polymer wall. Thus,  $\tau_r$  and  $\tau_d$  are improved. Moreover, the phase separation is clearly conducted since the liquid crystalline compound is fixed to the interface between the polymer wall and the liquid crystal region.

In the case where a mixture containing ferroelectric liquid crystal as a liquid crystal material and a polymerizable compound material which contains a liquid crystalline compound having a polymerizable functional group and an optically active group in its molecule is used, liquid crystal molecules having an optically active functional group are present at the interfaces between the polymer walls and the liquid crystal regions. Due to the presence of the liquid crystalline molecules, the liquid crystal regions are influenced by the ability of the polymer walls as well as that of the substrate. That is, the orientation regulating ability of the substrate (subjected to an orientation treatment) and that of the polymer walls (which have a component in a direction orthogonal to the surface of the substrate) influence the liquid crystal regions. Thus, the orientation of the

liquid crystal molecules is stabilized to improve shock resistance.

Furthermore, in the case where a mixture containing a liquid crystal material of a fluorine type and/or a chlorine type and a polymerizable compound which contains a polymerizable liquid crystalline compound having a fluorine atom(s) and/or a chlorine atom(s) in its molecule is used, liquid crystal molecules are chemically stabilized. Due to the chemical stability, a charge holding type element such as a TFT can be applied to the liquid crystal display device of the present invention without decreasing the electrical holding ratio of an entire display device.

#### 10 Application 30

Application 30 is the case where the orientation regulating ability of a polymer with respect to liquid crystal is increased. In this case, a mixture containing a polymerizable material having a liquid crystalline functional group and a liquid crystal material is used, whereby a phase separation of the mixture containing a curable material and liquid crystal is achieved in a liquid crystal phase. Thus, the polymer walls as well as the liquid crystal regions can be in an orientation state.

Hereinafter, a method for manufacturing a liquid crystal display device of Application 30 will be described.

First, the compound X used in Application 28 was prepared. Then, a homeotropic orientation film (JALS-203-R6, manufactured by Nippon Synthetic Rubber Co., Ltd.) was coated onto a glass substrate (1.1 mm thickness) with ITO (a mixture of indium oxide and tin oxide having a thickness of 500 Angstroms) as transparent electrodes by a spin coating method. After that, the substrate was baked. Two substrates treated in this way were made to face each other with spacers sandwiched therebetween so as to give a gap of 6  $\mu\text{m}$ . Thus, a cell was formed.

Then, a photomask having square masking portions was placed on the cell so that the masking portions covered the pixels. Each square masking portion had a side of 200  $\mu\text{m}$  and were provided at an interval of 50  $\mu\text{m}$  therebetween (i.e., the masking portions were disposed at a pitch of 250  $\mu\text{m}$ ). Moreover, a mixture containing 0.1 g of acrylate with two functional groups, i.e., a photopolymerizable compound (R-684, manufactured by Nippon Kayaku K.K.), 0.05 g of styrene, 0.85 g of the compound X, 4 g of a liquid crystal material (ZLI-2806, where anisotropy of dielectric constant  $\Delta\epsilon$  is  $< 0$ ; manufactured by Merck & Co., Inc.), and 0.0025 g of a photopolymerization initiator (Irgacure 651) was prepared.

The mixture thus prepared was observed by a polarizing microscope while varying temperature, revealing that the transition temperature at which liquid crystal was changed to nematic liquid crystal was 45°C and a transition temperature at which nematic liquid crystal was changed to a homogeneous liquid was 78°C. The mixture was injected into the cell at 48°C (in a nematic state). After that, the cell was irradiated with UV-rays through the photomask by using a high-pressure mercury lamp which can provide parallel rays under the condition that a cycle including one second irradiation and 30 seconds non-irradiation was repeated 20 times at 10 mW/cm<sup>2</sup> and 48°C. Then, the cell was continuously irradiated for 10 minutes. Moreover, the cell was irradiated without the photomask for 10 minutes, whereby the polymerizable compound contained in the mixture was cured.

One substrate was peeled off from the other substrate in liquid nitrogen, and the liquid crystal material was washed away with acetone. After that, a horizontal section of the polymer walls was observed by the SEM, confirming that the liquid crystal regions with the same regularity as that of a dot pattern of the photomask (i.e., the same regularity of the pixels) were formed, each liquid crystal region having almost the same size.

Two polarizing plates were attached to the upper and lower sides of the cell so that each polarizing direction crossed each other at right angles, whereby an ECB liquid crystal display device, in which the liquid crystal regions were partitioned by the polymer walls, was manufactured.

#### Application 31

Application 31 is within the scope of Application 29 or 30. A liquid crystal display device of Application 31 was manufactured as follows:

First, a cell was formed in the same way as in Application 30. The same mixture as that of Application 30 was injected into the cell. Then, the mixture was kept at 100°C, at which temperature the mixture became homogeneous. A photomask was placed on the cell in the same way as in Application 30 and the cell was irradiated with UV-rays. Finally, two polarizing plates were attached to the cell in the same way as in Application 30.

Comparative Example 27

The same orientation film as that of Application 30 was formed on the same substrate as that of Application 30, and the orientation film was subjected to a rubbing treatment by a nylon cloth. Then, the two substrates thus treated were made to face each other in the same way as in Application 30 so that the directions of the orientation films which are not in parallel with each other was obtained. After that, only the same liquid crystal material (ZLI-2806) as that of Application 30 was injected between the substrates, whereby a cell was formed. Two polarizing plates were attached to the upper and lower sides of the cell so that each polarizing direction crossed the other at right angles, whereby a conventional ECB display device was obtained.

Comparative Example 28

A cell was formed in the same way as in Application 30. The same mixture as that of Application 30 was injected into the cell, and then the cell was irradiated with UV-rays in the same way as in Application 30 without a photomask. Two polarizing plates were attached to the cell in the same way as in Application 30, whereby a polymer dispersed liquid crystal display device was manufactured.

Table 18 shows the electro-optic characteristics of the above-mentioned liquid crystal display devices. In an item of Inversion phenomenon in half tone, a mark ○ shows a state in which inversion phenomenon is not caused, a mark × shows a state in which inversion phenomenon is easily observed, and a mark Δ shows a state in which inversion phenomenon is barely observed.

Table 18

Comparison of electro-optic characteristics				
	Application 30	Application 31	Comparative Example 27	Comparative Example 28
Contrast	33	23	39	17
Inversion phenomenon in half tone	○	○	×	Δ

As is understood from Table 18, the liquid crystal display device of Application 30 is excellent in a black state under no applied voltage due to the homeotropic orientation of the polymer portions, and has an electro-optic characteristic comparable to that of the liquid crystal display device of Comparative Example 27. Moreover, in Application 30, a film substrate can also be used. Compared with the polymer dispersed liquid crystal display device of Comparative Example 28, the liquid crystal display device of Application 30 has higher contrast because of less light scattering in its pixels.

Furthermore, in Application 30, the liquid crystal molecules tilt in various directions due to the interaction with the polymer walls, so that the same refractive index can be obtained when seen from any direction, improving the viewing angle characteristic. In Comparative Example 27, the liquid crystal molecules tilt in one direction under an applied voltage, due to the rubbing treatment in one direction. Thus, the refractive index is varied depending upon the direction in which the liquid crystal molecules are seen, so that inversion phenomenon and change of contrast are caused depending upon the direction of the observation, deteriorating the viewing angle characteristic. In Comparative Example 28, liquid crystal regions in a particle shape were formed, and as a whole, a rough display was obtained.

The observation of the cell of Application 31 by a polarizing microscope revealed that the liquid crystal regions were in a nearly homeotropic orientation and light was passed through the polymer walls under crossed Nicols. Thus, contrast of the liquid crystal display device of Application 31 is slightly lower than that of Application 30.

Next, the reasons why a viewing angle characteristic is improved in Application 30 will be described.

A liquid crystal display device utilizing a conventional polarizing plate has a poor viewing angle characteristic. Thus, such a device is not suitable as a liquid crystal display device which is seen at a large angle (i.e., which is seen from various directions). For example, in the case where an initial orientation of liquid crystal molecules is a homeotropic orientation in an ECB liquid crystal display device, an orientation film is subjected to an orientation treatment so that the liquid crystal molecules tilt in one direction when applied with a voltage. Because of this, the liquid crystal molecules tilt in one direction in a half tone. Thus, when a liquid crystal mol-

ecule 121 is seen from an A direction and a B direction as shown in Figure 44A, each apparent refractive index is different, and contrast seen from the respective directions is greatly different. In some cases, a display defect such as inversion phenomenon is caused. In this way, the conventional liquid crystal display device has a poor viewing angle characteristic.

On the other hand, in a liquid crystal display device (with a polarizing plate) in which a phase separation between liquid crystal and a polymer material is regularly conducted by using a photomask, the liquid crystal molecule 121 tilts toward each polymer wall 126 under a voltage applied, due to the interaction between the liquid crystal molecule 121 and the polymer wall 126 as shown in Figure 44B. Thus, each apparent refractive index of a C direction and a D direction is almost the same, having great advantages in the improvement of a viewing angle characteristic. However, in this case, a very thin polymer film is formed between the liquid crystal molecules and the substrate in the liquid crystal regions, so that homeotropic orientation effects of the substrate are decreased, even though a homeotropic orientation film excellent in orientation regulating ability is used. Due to this, the homeotropic orientation of the liquid crystal molecules is slightly disturbed, and part of the light is passed through the cell under crossed Nicols, slightly decreasing contrast. Moreover, in the case of a mode utilizing a homeotropic orientation film, small liquid crystal droplets are formed in the polymer walls, the orientation state on the substrate is not reflected in the orientation of the liquid crystal molecules, and the liquid crystal molecules are in a random orientation. Therefore, part of the light is transmitted though the cell under crossed Nicols, remarkably decreasing apparent contrast. In the case of a ferroelectric liquid crystal display device, there is a problem of low shock resistance. This problem can be overcome by dispersing liquid crystal regions in the polymer walls; however, in this case, a phase separation is not clearly conducted making it difficult to regulate the orientation.

In Application 30, a homogeneous mixture containing a liquid crystal material and a polymerizable compound material (polymerizable compound having liquid crystallinity) is used and the polymerizable compound is cured in a liquid crystal state, whereby a phase separation is conducted between the liquid crystal and the polymer. According to this method, the liquid crystal and the polymer can be made in the same orientation state. In addition, if the polymerizable compound is cured in a liquid crystal state, the orientation state of the polymer walls as well as that of the liquid crystal regions can be maintained, so that the orientation of the liquid crystal regions becomes strong.

In particular, in the case of a general ECB liquid crystal display device, minute liquid crystal molecules are randomly aligned in the polymer walls, so that light is transmitted through the cell under crossed Nicols, decreasing contrast. On the other hand, in the case of Application 31, the liquid crystalline compound is contained in the polymer, and the compound has the same orientation as that of the liquid crystal material, so that light is hardly transmitted through the cell under crossed Nicols. Moreover, in the case of an ECB liquid crystal display device (with polarizing plates) to which Application 31 is applied, the liquid crystal molecules tilt in a random direction under an electrical field, due to the interaction between the polymer walls and the liquid crystal molecules. Therefore, the refractive index becomes the same, when seen from any direction, making the viewing angle characteristic in a half tone excellent.

#### Application 32

Application 32 is the case where contrast is improved, in addition to Application 30 in which the liquid crystal regions and the polymer walls have the same orientation state. In Application 32, a dichroic dye is used.

Hereinafter, a method for manufacturing a liquid crystal display device of Application 32 will be described.

A cell was formed so as to have a thickness of 9  $\mu\text{m}$  in the same way as in Application 30. A mixture was prepared in the same way as in Application 30, except that a liquid crystal material in which 4% of a dichroic dye (S-301, manufactured by Mitsui Toatsu Chemicals, Inc.) was added to ZLI-2806 was used. A mixture containing the liquid crystal material and the other materials (e.g., a photopolymerization initiator) was checked for its transition temperature by a differential scanning calorimeter (DSC), leading to almost the same results as those of Application 30. Then, the mixture was injected into the cell at 48°C and the cell was irradiated with UV-rays through a photomask, whereby the polymerizable material contained in the mixture was cured.

A substrate on which Al was vapor-deposited was placed on the cell thus obtained. Then, an optical source and an observation section were respectively placed in different positions at an angle of 30° from a vertical direction with respect to the cell, whereby an electro-optic characteristic as a reflective liquid crystal display device was measured.

In the cell thus obtained, as shown in Figure 45A, liquid crystal molecules 121 and a dichroic dye 122 in a liquid crystal region 127 and a polymer and the dichroic dye 122 in a polymer wall 126 were aligned in the same direction under no applied voltage, so that the whole area (i.e., the liquid crystal regions and the polymer walls) was in a colorless state. When a voltage was applied to electrodes 123, as shown in Figure 45B, the

liquid crystal molecules **121** and the dichroic dye **122** in the liquid crystal region **127** alone changed their orientation to be colored. In Figures **45A** and **45B**, the reference numeral **124** denotes a substrate, and **128** an orientation film. The contrast and saturation drive voltage of the liquid crystal display device of Application 32 were 7 and in the vicinity of 7 V, respectively. Moreover, the liquid crystal molecules tilt in an omnidirection under an applied voltage, so that contrast was uniform in an omnidirection.

#### Comparative Example 29

A liquid crystal display device was manufactured as follows:

A substrate was subjected to a rubbing treatment in one direction by using a nylon cloth in the same way as in Application 32. Two substrates thus obtained faced each other so that each orientation direction was in an anti-parallel state. Then, ZLI-2806 (containing 4% of a dichroic dye S-301) was injected into the cell. Thus, a conventional liquid crystal display device of a GH mode was manufactured. In this device, the liquid crystal molecules tilted in one direction under a voltage applied, so that contrast was varied depending upon the observation direction, decreasing display characteristics.

As described above, in the case of Applications 30 and 32, the polymerizable material is cured in a liquid crystal state, so that the orientation direction of the liquid crystal layer can artificially be determined. When the polymerizable material is cured in a non-liquid crystal state as in Applications 28 and 29, a very thin polymer film is formed between the substrate and the liquid crystal layer. Therefore, the orientation regulating ability of the substrate is decreased, making it difficult to artificially determine the orientation of the liquid crystal layer. Moreover, in Applications 28 and 29, the polymer is not aligned, so that minute liquid crystal molecules entered from the liquid crystal regions into the polymer walls are randomly aligned since the molecules are aligned along the polymer walls, causing problems. For example, in the case where the liquid crystal display device is used under crossed Nicols, utilizing a homeotropic orientation film, the minute liquid crystal molecules in the liquid crystal regions are randomly aligned, so that light leakage is generated to decrease contrast. In the case of Applications 30 and 32, due to the thin polymer film entered between the substrate and the liquid crystal regions, the polymer is also aligned to be cured in the orientation direction of the substrate; as a result, the liquid crystal regions are aligned in the orientation direction of the substrate.

The liquid crystal display devices of Applications 30 and 32 can be applied to conventional liquid crystal display devices which require an orientation treatment, such as TN, GH, STN, ECB and FLC liquid crystal display devices. In particular, applications in ECB, GH, FLC liquid crystal display devices are effective. For example, when the liquid crystal display devices of Applications 30 and 32 are applied to an ECB liquid crystal display device, the viewing angle characteristic can be improved. That is, in an ECB mode, liquid crystal molecules are in a homeotropic orientation under no applied voltage (black state under crossed Nicols). When a voltage is applied, the liquid crystal molecules tilt (a white state is obtained due to birefringence). The liquid crystal molecules tilt in various directions due to the interaction between the liquid crystal molecules and the polymer, so that the refractive index becomes the same in any directions, whereby the viewing angle characteristic can be improved.

Even in the case of the ECB liquid crystal display device (with no polarizing plate) in which a dichroic dye is added, when the polymer walls are not aligned, the dichroic dye contained in the polymer walls takes a colored state in a random orientation and the orientation of the dichroic dye is not changed with respect to the application of an electrical field, decreasing overall contrast. On the other hand, in the case where the polymer is also aligned as in Applications 30 and 32, the dichroic dye contained in the polymer walls can also be in a homeotropic orientation state. Thus, in the polymer walls, a nearly transparent state as a whole is changed to a state in which only the dichroic dye is colored, and the dichroic ratio of the dichroic dye can be used to the full. Moreover, when the polymerizable compound material is cured by using a photomask, since the dichroic dye is contained in the mixture, light is not leaked into masking portions of the photomask. Therefore, regions where the polymer walls are to be formed are clearly limited. Furthermore, in this case, due to the electrical field, the polymer walls and the orientation ability of the liquid crystal, the liquid crystal molecules in a vertical direction are aligned in a horizontal direction with respect to the cell and in a random direction within a surface horizontal with respect to the cell. Thus, a reflective liquid crystal display device excellent in viewing angle characteristic can be manufactured.

In the application to a GH mode using liquid crystal to which a dichroic dye is added, the vertical direction and the horizontal direction of the liquid crystal molecules can electrically be switched, so that a dichroic ratio of the dichroic dye can be used to the full. Moreover, the dichroic dye contained in the polymer walls are in a homeotropic orientation, so that its molecules are aligned in a direction to be colorless. Thus, a colorless state as a whole can be electrically changed into a state in which only liquid crystal regions are colored.

In the application to an FLC liquid crystal display device, the liquid crystal molecules are more strongly

aligned due to the uniaxially oriented polymer. Because of this, low shock resistance which is the most serious disadvantage of the FLC can be improved by the polymer walls. Furthermore, in the case where a FLC polymerizable material is used as a light-curable material, the FLC polymer also responds to the application of a voltage, and a half tone display can be realized because of the difference in the drive voltage between the FCL and the FLC polymer.

In Applications 30 and 32, the polymerizable material contained in the mixture is cured in a liquid crystal state. Examples of the liquid crystal state include a nematic phase, smectic phase, and a cholesteric phase.

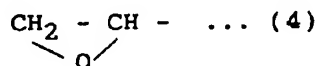
Hereinafter, materials applicable to the present examples will be described.

(A polymerizable liquid crystalline compound)

As a polymerizable liquid crystalline compound, the compound X is used In Applications 28, 30 and 32 and the compound Y is used in Application 29. The present invention is not limited thereto. A general compound represented by the following Formula (3) can be used.

A - B - LC (3)

In Formula (3), Letter A represents a polymerizable functional group. Examples thereof include functional groups having unsaturated bonds such as  $\text{CH}_2=\text{CH}-$ ,  $\text{CH}_2=\text{CH}-\text{COO}-$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-$ , and  $-\text{N}=\text{C}=\text{O}$ , and functional groups having a heterocyclic structure with strain such as a structure represented by the following Formula (4).



Letters LC represent a liquid crystalline compound. Examples thereof include a compound represented by the following Formula (5), a cholesterol ring, and derivatives thereof.

D - E - G (5)

Letter B represents a coupling group connecting the polymerizable functional group to the liquid crystalline compound. Examples thereof include an alkyl chain ( $-(\text{CH}_2)_n-$ ), an ester bond ( $-\text{COO}-$ ), an ether bond ( $-\text{O}-$ ), a polyethylene glycol chain ( $-\text{CH}_2\text{CH}_2\text{O}-$ ), and coupling groups obtained by combining these coupling groups. In particular, in order that the liquid crystalline compound can easily move on the polymer walls in response to the electrical field, a coupling group having 6 or more bonds from the polymerizable functional group to the fixed portion of the liquid crystal molecules is preferred.

In the case where the polymer walls are also aligned, it is preferred that the liquid crystalline compound exhibits liquid crystallinity when mixed with the liquid crystal material.

In Formula (5), Letter D represents a functional group capable of being bound to the coupling group represented by Letter B, and has a function of influencing the degree of anisotropy of dielectric constant of the liquid crystal molecules and that of the anisotropy of refractive index. Examples thereof include a p-phenyl ring, a 1,10-diphenyl ring, a 1,4-cyclohexane ring, a 1,10-phenylcyclohexane ring, a naphthalene ring, and a tarphenyl ring. G represents a polar group which makes the anisotropy of dielectric constant of the liquid crystal exhibited. Examples thereof include a benzene ring, a cyclohexane ring, a p-diphenyl ring, a phenylcyclohexane ring, a tarphenyl ring, and a diphenylcyclohexane ring, each having a functional group such as  $-\text{CN}$ ,  $-\text{OCH}_3$ ,  $-\text{F}$ ,  $-\text{Cl}$ ,  $-\text{OCF}_3$ ,  $-\text{OCCl}_3$ ,  $-\text{H}$ ,  $-\text{R}$  (R: alkyl group). E represents a functional group connecting D to G. Examples thereof include a single bond,  $-\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{O}-$ , a triple bond of carbon-carbon, and  $-\text{CH}=\text{CH}-$ .

(A liquid crystal material)

The liquid crystal material as that of Example 2 can be used.

(A polymerizable material)

A light-curable material (photopolymerizable material), a thermosetting material (heat-polymerizable material), and the like can be used. As a light-curable material, there are acrylic acids and acrylic esters having a long chain alkyl group with three or more carbons or having a benzene ring. Examples of the light-curable material include isobutyl acrylate, stearyl acrylate, lauryl acrylate, isoamyl acrylate, n-butyl methacrylate, n-lauryl methacrylate, tridecyl methacrylate, 2-ethylhexyl acrylate, n-stearyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-phenoxyethyl methacrylate, isobornyl acrylate, and isobornyl methacrylate. In addition, in order to increase the physical strength of the polymer, multi-functional materials having two or

more functional groups can be used. Examples of the mult-functional materials include bisphenyl A dimethacrylate, bisphenol A diacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, trimethylol propane trimethacrylate, trimethylol propane triacrylate, tetramethylolmethane tetraacrylate, and neopentyl diacrylate. More preferably, material obtained by halogenating, in particular, chlorinating or fluorinating these monomers are used. Examples thereof include 2,2,3,4,4,4-hexafluorobutyl methacrylate, 2,2,3,4,4, 4-hexachlorobutyl methacrylate, 2,2,3,3-tetrafluoropropyl methacrylate, 2,2,3,3-tetrafluoropropyl methacrylate, perfluorooctylethyl methacrylate, perfluorooctylethyl methacrylate, perfluorooctylethyl acrylate, and perfluorooctylethyl acrylate.

As the thermosetting compound, the above-mentioned light-curable materials and compounds having an epoxy group, an isocyanate group, etc. in its molecules can be used. Examples of the light-curable compound include bisphenol A type epoxy compounds, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, hexahydrobisphenol A diglycidyl ether, propylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, diglycidyl ester phthalate, triglycidyl isocyanate, and tetraglycidylmethoxymethylene diamine.

These monomers can be used alone or in a combination of two or more kinds. Moreover, compounds which have both a light-curable property and heat-curable property can be used. Among the light-curable or heat-curable compounds, in the case where fluorinated compounds having the effects of reducing hysteresis and increasing the response speed are used, the interaction between the liquid crystal regions and the polymer walls can be decreased.

As the dichroic dye used in the present invention, both N-type and P-type dyes can be used. Examples of the dichroic dye include a merocyanine type, an anthraquinone type, a styryl type, and an azobenzene type. The added amount of the dichroic dye is in the range of 0.5% to 10% by weight based on the weight of the liquid crystal, preferably in the range of 1% to 5%. Moreover, it is also possible to use another dye for coloring together with the dichroic dye; however, in some cases, sufficient contrast cannot be obtained due to the light absorption effects.

When the liquid crystalline compound having a polymerizable functional group in its molecule is selected, it is preferred in terms of compatibility that portions exhibiting liquid crystallinity of the liquid crystal material and those of the polymerizable liquid crystalline compound are similar to each other. In particular, when a fluorine and/or chlorine type liquid crystal material (which has specific chemical environment) is used, it is preferred that a fluorine and/or chlorine type liquid crystal material is used as a liquid crystalline compound having a polymerizable functional group. Moreover, in the case where ferroelectric crystal is used, a polymerizable compound having ferroelectric liquid crystal in its molecule is preferred for forming a stable smectic phase.

(The weight ratio of liquid crystal and a polymerizable compound)

The weight ratio of the liquid crystal and the polymerizable compound is preferably in the range of 50:50 to 97:3, more preferably in the range of 70:30 to 90:10. When the percentage of the liquid crystal material is less than 50%, the ratio occupied by the polymer walls increases, resulting in a remarkable rise in the drive voltage of the cell. Thus, practicality is lost. In contrast, when the percentage of the liquid crystal material is more than 97%, the physical strength of the polymer walls decreases. Thus, stable performance cannot be obtained.

Moreover, in the case where a polymerizable liquid crystalline compound and a polymerizable non-liquid crystalline compound are mixed, it is preferred that the weight ratio thereof is within the above-mentioned range and the percentage of the polymerizable liquid crystalline compound is 0.5% or more. In particular, in the case where ferroelectric liquid crystal is used, a ferroelectric liquid crystal display device capable of performing a half tone display can be manufactured as follows:

The percentage of the polymerizable liquid crystalline compound is made 70% or more, whereby two regions, i.e., a low molecular liquid crystal region and a polymer liquid crystal region are formed. Then, a voltage is adjusted to a value at which each compound is driven.

(A photopolymerization initiator or catalyst)

A reaction initiator includes a photopolymerization initiator, a heat polymerization initiator, etc. As the photopolymerization initiator, Irgacure 184, Irgacure 651, Irgacure 907, Darocure 1173, Darocure 1116, Darocure 2959, and the like can be used. As the heat polymerization initiator, peroxides such as biphenyl peroxide and t-butyl peroxide; and a radical generating agent such as AIBN can be used. Moreover, the added amount of the polymerization initiator(s) is varied depending upon the reactivity of each compound. There is no special limit in the present example. It is preferred that the added amount of the photopolymerization initiator(s) is in the range of 0.01% to 5% based on the total amount of a mixture of liquid crystal and a light-curable material

(containing polymerizable liquid crystalline material). When the added amount is more than 5%, the phase separation speed between the liquid crystal and the polymer is too high to be regulated. As a result, liquid crystal regions become small, the drive voltage is increased, the orientation regulating ability of the orientation film on the substrate is decreased, less liquid crystal regions are formed in pixels (liquid crystal regions are formed in the masking portions in the case where a photomask is used), and contrast is decreased. In contrast, when the added amount is less than 0.01%, the polymerizable material cannot be sufficiently cured.

(An orientation film)

As a material for the orientation film, organic films such as polyimide (SE 150, manufactured by Nissan Chemical Industries Ltd.; Cytop, manufactured by Asahi Glass Co., Ltd., etc.) and inorganic films such as SiO can be used. If required, the orientation film is subjected to a rubbing treatment.

In Example 11, items described in Example 2: A light regulating means such as a photomask, Irradiation light, etc. can be applicable.

#### Example 12

Example 12 is the case where the response speed and the electrical holding ratio of a non light scattering type liquid crystal display device are increased by taking advantage of the mixture.

The mixture to be used in the liquid crystal display device of the present example is formed of a liquid crystal material, a polymerizable liquid crystalline compound, a photopolymerizable compound, and a photopolymerization initiator; or a liquid crystal material, a polymerizable liquid crystalline compound, a heat polymerizable compound, and a heat polymerization initiator.

The liquid crystal material and the polymerizable liquid crystalline compound are selected so that the product of anisotropy of dielectric constant  $\Delta\epsilon_L$  and a polymerizable liquid crystal compound  $\Delta\epsilon_P$  (i.e.,  $\Delta\epsilon_L \cdot \Delta\epsilon_P$ ) becomes negative. The purpose of this condition is that a liquid crystalline polymer is supported by polymer walls when the photo- or heat-polymerizable compound and the polymerizable liquid crystalline compound are cured. In this structure, the interfaces between the liquid crystal regions and the polymer walls are driven under an applied voltage. When a voltage is not applied, the interaction between the liquid crystalline polymer and the polymer walls is increased since the end portions (polymerizable functional groups) of the liquid crystalline polymer and the polymer walls are bonded to each other. Then, the orientation is disturbed between the liquid crystalline polymer and the liquid crystal molecules in the liquid crystal regions, so that the liquid crystal molecules immediately return to the orientation in a light scattering state. As a result, the response speed of the liquid crystal display device can be improved. The anisotropy of dielectric constant is an intrinsic property of the liquid crystalline functional group and does not change before and after the polymerization reaction, so that the anisotropy of the dielectric constant of the polymerizable liquid crystalline compound and that of the polymerized liquid crystalline compound are the same. Moreover, even in the case where the liquid crystal material and the polymerizable liquid crystalline compound which have a fluorine atom(s) and/or a chlorine atom(s) in its molecule and have a weak interaction therebetween are used, an element of a charge holding type such as a TFT can be applied to the liquid crystal display device due to the chemical stability inherent in these materials without decreasing the electrical holding ratio of the device itself.

In the case where the polymerizable liquid crystalline compound and the heat polymerizable compound are thermally polymerized in the present example, if a response speed is low, polymerized ends are formed in the liquid crystal regions, resulting in the formation of the polymer walls in the liquid crystal regions and decreasing contrast. Thus, it is preferred that the reaction system and reaction conditions which make the polymerization reaction complete within 10 minutes are selected.

Hereinafter, materials and the like applicable to the present example will be described.

(A polymerizable material)

The respective polymerizable compounds described: A polymer material in Example 11 can be used as the photopolymerizable compound and the heat polymerizable compound.

(A weight ratio of the liquid crystal material with respect to the polymerizable compound, etc.)

The mixed ratio of the liquid crystal material with respect to the polymerizable liquid crystalline compound and the photo- or heat-polymerizable compound is preferably in the range of 50:50 to 97:3 (weight ratio), more preferably in the range of 70:30 to 90:10 (weight ratio). When the mixed ratio of the liquid crystal material is



less than 50% by weight, a great number of polymer walls are formed, remarkably increasing the drive voltage of the liquid crystal display device, resulting in a loss of practicability of the device. When the mixed ratio of the liquid crystal material is more than 97% by weight, the physical strength of the polymer walls to be formed is decreased, making it difficult to obtain stable performance. Thus, these cases are not preferred. Under the condition of the above-mentioned range, it is preferred that the polymerizable liquid crystalline compound is made 0.05% or more by weight based on the total weight of the polymerizable liquid crystalline compound and the photo- or heat-polymerizable compound.

#### 10 (A polymerization initiator)

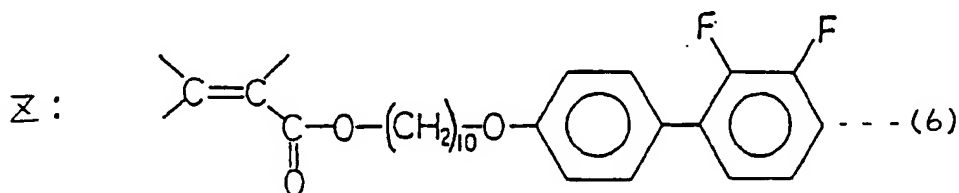
A general photo- or heat-polymerization initiator can be used. Examples of the photopolymerization initiator include Irgacure 184, Irgacure 651, Irgacure 907, Darocure 1173, Darocure 1116, Darocure 2959, etc. Examples of the heat polymerizable initiator include peroxides such as benzoperoxide (BPO), t-butyl peroxide; and azo compounds such as azobis(isobutyronitrile) (AIBN). It is preferred that the mixed ratio of the photo- or heat-polymerizable initiator is in the range of 0.3 to 5% by weight based on the total weight of the liquid crystal material, the polymerizable liquid crystalline compound and the photo- or heat-polymerizable compound. When the mixed ratio is less than 0.3% by weight, there is a possibility that the polymerization reaction does not sufficiently start. Thus, this ratio is not preferred. When the mixed ratio is more than 5% by weight, the phase separation speed between the liquid crystal and the polymer is too high to regulate the size of the liquid crystal regions; as a result, small liquid crystal regions are formed, increasing the drive voltage. Thus, this ratio is not preferred.

The present example will be described by way of illustrating Applications.

#### 25 Application 33

The liquid crystal display device of Application 33 has the same structure as that shown in Figure 35. A method for manufacturing this liquid crystal display device is as follows:

First, a polymerizable liquid crystalline compound Z (with the anisotropy of dielectric constant  $\Delta\epsilon < 0$ ) shown by the following Formula (6) was prepared in the following manner: 4'-hydroxy-2, 3-difluorobiphenyl and excess 1,10-dibromodecane were etherificated in the presence of calcium carbonate. The resulting ether was purified by column chromatography. After that, the purified substance was mixed with equimolar tetramethylammoniumhydroxypentahydrate, and acrylic acid was added to this mixture to obtain the polymerizable liquid crystalline compound Z represented by Formula (6):



Next, the electrode lines 73 and 74 made of ITO (a mixture of indium oxide and tin oxide) were formed on the substrates 71 and 72, respectively. In the present application, a PET film with a thickness of 0.25 mm was used as the substrates 71 and 72, and the electrode lines 73 and 74 respectively having a width of 200  $\mu\text{m}$  were formed with an interval of 50  $\mu\text{m}$  between each electrode line. The respective number of the electrode lines 73 and 74 was 20. Then, the orientation films 75 and 76 were coated so as to cover the electrode lines 73 and 74 by a spin coating method. The orientation films 75 and 76 were subjected to a rubbing treatment in one direction. In Application 33, polyimide (SE150, manufactured by Nissan Chemical Industries Ltd.) was used as the orientation films 75 and 76. These substrates 71 and 72 face each other with spacers having a diameter of 6  $\mu\text{m}$  sandwiched therebetween so that the electrode lines 73 and 74 faced and crossed each other. Thus, a liquid crystal cell was formed.

Next, the photomask 79 was placed outside the substrate 72 so that masking portions of the photomask 79 covered the pixels. Then, 0.85 g of a photopolymerizable compound, 0.05 g of the polymerizable liquid crystalline compound Z, 4 g of a liquid crystal material, and 0.15 g of a photopolymerization initiator were homogeneously mixed to obtain a mixture 80. The mixture 80 was injected into the cell. In Application 33, as the photopolymerizable compound, 0.1 g of trimethylol propane trimethacrylate, 0.30 g of 2-ethylhexyl acrylate,

and 0.45 g of isobornyl acrylate were used. As the liquid crystal material, a mixture in which 0.3% of cholesteric nanonate (CN) was added to ZLI-4792 (manufactured by Merck & Co., Inc., where the anisotropy of dielectric constant is  $\Delta\epsilon > 0$ ) was used. As the photopolymerization initiator, Irgacure 184 was used.

Then, the cell was irradiated with UV-rays through the photomask 79 at 10 mW/cm<sup>2</sup> for 5 minutes by using a high-pressure mercury lamp which can provide parallel rays, whereby the photopolymerizable compound and the polymerizable liquid crystalline compound were cured.

One substrate was peeled off from the other substrate in liquid nitrogen. Then, the liquid crystal material was washed away with acetone. A cross-section of the polymer walls was observed by the SEM, revealing that liquid crystal regions with the same regularity as that of the photomask 79 (i.e., the same regularity as that of the pixel distribution) were uniformly formed, each liquid crystal region having almost the same size.

Two polarizing plates were attached to the cell thus obtained so that the respective polarizing directions were aligned with the orientation directions of the corresponding orientation films, whereby a TN liquid crystal display device was obtained.

#### Comparative Example 30

Glass with ITO (flint glass with ITO having a thickness of 500 Angstroms, manufactured by Nippon Sheet Glass Co., Ltd.) was used as the substrates 71 and 72 of Application 33. A liquid crystal material (ZLI-4792 to which 3% of CN was added, manufactured by Merck & Co., Inc., where the anisotropy of dielectric constant is  $\Delta\epsilon > 0$ ) was injected into the liquid crystal cell, whereby a conventional liquid crystal display device which was not a polymer dispersed type was manufactured.

#### Comparative Example 31

A liquid crystal display device was manufactured in the same way as in Application 33, except that the photomask 79 was not used.

Table 19 shows a comparison of contrast characteristics obtained in Application 33, and Comparative Examples 30 and 31. Contrast is taken as  $T_0/T_{sat}$ , where  $T_0$  is light transmittance obtained under no applied voltage and  $T_{sat}$  is light transmittance obtained under an applied saturation voltage. Here, light transmitted through a liquid crystal panel is detected by a detector with a converging angle of 6°, using a metal halide lamp as an optical source, whereby contrast is measured.

Table 19

Comparison of contrast characteristics			
	Application 33	Comparative Example 30	Comparative Example 31
Contrast	41	41	9

As is understood from Table 19, the liquid crystal display device of Application 33 has an electro-optic characteristic comparable to that of the conventional liquid crystal display device of Comparative Example 30. In addition, in Application 33, the polymer walls can be formed having a regularity with respect to the pixels by using the photomask. Compared with the liquid crystal display device of Comparative Example 31 manufactured without using a photomask, the number of the interfaces between the polymer walls and the liquid crystal regions are greatly decreased, so that light scattering is sufficiently reduced between the polymer walls and the liquid crystal regions.

#### Application 34

A liquid crystal cell was formed in the same way as in Application 33, except that glass with ITO (flint glass with ITO having a thickness of 500 Angstroms, manufactured by Nippon Sheet Glass Co., Ltd.) was used as the substrates 71 and 72 and plastic beads with a diameter of 12  $\mu$ m were sandwiched as spacers between the substrates 71 and 72.

Then, the photomask 79 was placed in the same way as in Application 33. The mixture 80 was prepared in the same way as in Application 33, except that 0.01 g of trimethylol propane trimethacrylate and 0.08 g of isobornyl acrylate as the photopolymerizable compound, 0.01 g of the polymerizable liquid crystalline compound Z, 0.4 g of ZLI-4792 (manufactured by Merck & Co., Ltd., where the anisotropy of dielectric constant is

$\Delta\epsilon > 0$ ) as the liquid crystal material, and 0.015 g of Irgacure 651 as the photopolymerization initiator were used. Then, the cell was irradiated with UV-rays through the photomask 79 at 40 mW/cm<sup>2</sup> for 2 minutes by using a high-pressure mercury lamp, whereby the polymerizable compound and the polymerizable liquid crystalline compound were cured to obtain a liquid crystal display device.

#### Comparative Example 32

A liquid crystal display device was manufactured in the same way as in Application 34, except that a mixture containing 0.01 g of trimethylol propane trimethacrylate and 0.09 g of isobornyl acrylate as the photopolymerizable compound, 0.4 g of ZLI-4792 (manufactured by Merck & Co., Inc., where the anisotropy of dielectric constant is  $\Delta\epsilon > 0$ ) as the liquid crystal material, and 0.015 g of Irgacure 651 as the photopolymerization initiator was used instead of the mixture 80 used in Application 34.

#### Comparative Example 33

A liquid crystal display device was manufactured in the same way as in Application 34, except that a mixture containing 0.01 g of trimethylol propane trimethacrylate and 0.09 g of isobornyl acrylate as the photopolymerizable compound, 0.4 g of E7 (manufactured by Merck & Co., Inc., where the anisotropy of dielectric constant is  $\Delta\epsilon > 0$ ) as the liquid crystal material, and 0.015 g of Irgacure 651 as the photopolymerization initiator was used instead of the mixture 80 used in Application 34.

Table 20 shows the results obtained by measuring contrast, response speed, and the electrical holding ratio of the liquid crystal display device of Application 34 and those of Comparative Examples 32 and 33. The contrast is taken as  $T_{\text{sat}}/T_0$  (converging angle: 6°) in the same way as in Application 33. The response speed is taken as the sum of times  $\tau_r$  and  $\tau_d$ , where  $\tau_r$  is the time required for light transmittance to change from  $T_0$  to  $0.9 \times T_{\text{sat}}$  while the voltage is increased from 0 to 10 V, when a voltage is applied to a liquid crystal panel by being changed from 0 V→10 V→0 V; and  $\tau_d$  is a time required for light transmittance to change from  $T_{\text{sat}}$  to  $0.9 \times T_0$  while a voltage is changed from 10 V to 0 V, when a voltage is applied to a liquid crystal panel by being changed from 0 V→10 V→0 V. If this value is smaller, the response speed is higher. The electrical holding ratio is taken as a ratio of the amount of charge retained for 16.5 ms with respect to the initial charge amount, when 5 V voltage with a rectangular wave is applied to the liquid crystal panel. For example, when the charge is not leaked out of the liquid crystal panel at all, the electrical holding ratio is 100%.

Table 20

Comparison of electro-optic characteristics			
	Application 34	Comparative Example 32	Comparative Example 33
Contrast	8	8	-
Response speed (ms)	45	185	-
Electrical holding ratio (%)	98.2	98.0	82.4

As is understood from Table 20, the liquid crystal display device of Application 34 has a high response speed and a satisfactory electrical holding ratio. However, the liquid crystal display device of Comparative Example 32 has a low response speed. In Comparative Example 33, the drive voltage of the liquid crystal display device is 20 V or more, so that contrast and a response speed cannot be measured, and its electrical holding ratio is not satisfactory.

Hereinafter, materials and the like applicable to Applications 33 and 34 will be described.

(A liquid crystal material)

The liquid crystal material described:

A liquid crystal material in Example 2 can be used.

(A polymerizable liquid crystalline compound)

The polymerizable liquid crystal line compound described: A polymerizable liquid crystalline compound in  
 5 Example 11 can be used.

In the case where the polymerizable liquid crystal line compound used in the present example has positive  
 anisotropy of dielectric constant ( $\Delta\epsilon_L > 0$ ), a functional group of the compound G represented by Formula (5)  
 is positioned so that anisotropy of dielectric constant  $\Delta\epsilon_P$  of the polymerizable liquid crystalline compound be-  
 comes negative. Examples of the compound G having such a functional group include 2-substitution product,  
 10 3-substitution product, 2,3-substitution product, etc. of a benzene ring. In the case where the liquid crystal ma-  
 terial has negative anisotropy of dielectric constant  $\Delta\epsilon_L < 0$ , a functional group of the compound G is positioned  
 so that the anisotropy of dielectric constant  $\Delta\epsilon_P$  of the polymerizable liquid crystalline compound becomes pos-  
 itive. Examples of compounds having such a functional group include 4-substitution product, 3,4,5-substitution  
 product, 3,4-substitution product, etc. of a benzene ring. When a plurality of functional groups of these substi-  
 15 tution products are present in the same substitution product, the kind of a plurality of functional groups is not  
 limited to one. Moreover, in either of the above-mentioned cases, only one kind of the polymerizable liquid crys-  
 talline compound can be used or a plurality of the polymerizable liquid crystalline compounds can be used.  
 When the polymerizable liquid crystalline compound having the above-mentioned structure is polymerized, a  
 liquid crystalline polymer obtained as a result of the polymerization has a liquid crystalline functional group LC  
 20 in liquid crystal regions and a polymerizable functional group A in polymer walls, whereby the liquid crystalline  
 polymer is fixed on the polymer walls.

(Conditions for selecting a liquid crystal material and a polymerizable liquid crystalline compound)

25 It is preferred in terms of compatibility that the liquid crystal material and the polymerizable liquid crys-  
 talline compound are selected so that respective portions exhibiting liquid crystallinity are similar to each other.  
 In particular, in the case where a liquid crystal material of a fluorine type and/or a chlorine type, which has an  
 intrinsic chemical environment, is selected, it is preferred to select a polymerizable liquid crystalline compound  
 of a fluorine type and/or a chlorine type.

30

#### Application 35

First, 0.1 g of the polymerizable liquid crystalline compound Z of Application 33 and 0.01 g of benzoperoxide  
 (BPO) were dissolved in toluene, followed by being polymerized at 100°C for 2 hours. Then, ethanol was added  
 35 to this mixture to obtain a polymer. The polymer thus obtained was washed with ethanol to obtain a liquid crys-  
 talline polymer Z' (which is a polymer of the polymerizable liquid crystalline compound Z).

Next, 2 g of E8 (manufactured by Merck & Co., Inc., where the anisotropy of dielectric constant is  $\Delta\epsilon > 0$ )  
 and 0.01 g of the liquid crystalline polymer Z' as a liquid crystal material, and 0.5 g of polymethyl methacrylate  
 (PMA, manufactured by Asahi Kasei Kogyo K.K.) as a polymer other than the liquid crystalline polymer were  
 40 dissolved in chloroform, whereby a solution with a solute concentration of 15% by weight was prepared. This  
 solution was coated onto the substrate 71 by a bar coating method, followed by being dried to form a film with  
 a thickness of 12 to 13  $\mu\text{m}$ . After that, the substrate 72 was placed on the substrate 71 to obtain a liquid crystal  
 panel. In Application 35, glass with ITO (flint glass with ITO having a thickness of 500 Angstroms, manufactured  
 by Nippon Sheet Glass Co., Ltd.) was used as the substrates 71 and 72.

45

#### Comparative Example 34

A liquid crystal display device was manufactured in the same way as in Application 35, except that the  
 liquid crystalline polymer Z' was not used.

50 Table 21 shows the results obtained by measuring contrast and response speed of the liquid crystal display  
 devices of Application 35 and Comparative Example 5. The response speed is measured in the same way as  
 in Application 34, except that the 10 V voltage in Application 34 is made 20 V. The contrast is measured in the  
 same way as in Application 33.

55

Table 21

Comparison of electro-optic characteristics		
	Application 35	Comparative Example 34
Contrast	70	69
Response speed (ms)	53	202

As is understood from Table 21, the liquid crystal display device of Application 35 has satisfactory contrast and a high response speed. On the other hand, the liquid crystal display device of Comparative Example 34 has a low response speed.

In the manufacturing of the liquid crystal display device of Application 35, a mixture to be coated onto one substrate is formed from a liquid crystal material, a polymerizable liquid crystalline material, and a solvent which homogeneously dissolves the liquid crystal material and the polymerizable liquid crystalline material. After this mixture is coated onto one substrate, the solvent is removed by evaporation from the mixture.

In Application 35, a liquid crystal material and a liquid crystalline polymer which satisfy the same conditions as those applied to the liquid crystal material and the polymerizable liquid crystalline compound in Applications 33 and 34 were used. Examples of the liquid crystal material used in Application 35 include E7 and E8 (manufactured by Merck & Co., Inc.). Examples of the liquid crystalline polymer used in Application 35 include polymers having a liquid crystalline functional group attracted to a side chain, which are disclosed in Japanese Laid-Open Patent Publication No. 3-195796. Preferably, polymerized liquid crystalline compounds used for manufacturing the liquid crystal display device of Application 33 can be used.

Examples of the solvent include chloroform, toluene, xylene, and cyclohexane. It is preferred that the solvent is mixed in an amount in the range of 0.01 to 10% by weight.

In addition to the above-mentioned polymerizable liquid crystalline compounds, if required, it is possible to add polymers such as polystyrene, polyvinyl alcohol, polyvinyl acetate, methyl polymethacrylate, nitrocellulose, polycarbonate, polyphenylene oxide, polymethyl methacrylate (PMMA), etc. for the purpose of improving the physical strength of the polymer walls. In Application 35, polymethyl methacrylate is added. It is preferred that the mixed ratio of the polymer for improving the physical strength of the polymer walls is 0.1% by weight based on the total weight of the liquid crystalline polymer and the polymer for improving the physical strength of the polymer walls.

A liquid crystal display device with a structure in which the liquid crystal is confined in the polymer walls (or the liquid crystal is partially partitioned by the polymer walls) can be obtained by sandwiching the liquid crystal cell of the present example by two polarizing plates. This liquid crystal display device can be applied to conventional display systems such as TN, STN, FLC (SSF) and ECB systems. In addition, in the present example, a large screen and a substrate in a film shape are made possible.

In Example 12, items described in Example 2: A light regulating means such as a photomask, Irradiation light, etc. can be applicable.

#### Example 13

In Example 13, peeling phenomenon between the substrate and the polymer dispersed liquid crystal material, which has been a problem in a conventional polymer dispersed liquid crystal display device, is prevented, response speed is made high, and hysteresis is reduced by decreasing monomers remaining in a liquid crystal display device.

First, a mixture injected between facing substrates is irradiated with UV-rays. The mixture contains a liquid crystal material, a photosetting compound, a photopolymerization initiator, and a radical generating agent. Due to this, a display medium in which liquid crystal droplets are dispersed in polymer walls can be obtained. After that, the display medium is heated to thermally decompose the radical generating agent. As a result, a radical is generated from the radical generating agent, and a remaining monomer before heating is polymerized by the radical to decrease the remaining monomer.

The polymer dispersed liquid crystal display device of Example 13 has the same structure as that shown in Figure 35. This device is manufactured as follows:

First, the electrode lines 73 and the orientation film 75 are formed on the substrate 71, and the electrode lines 74 and the orientation film 76 are formed on the substrate 72. Alternatively, the substrates 71 and 72 which have the above-mentioned structures are provided.

Next, the substrates **71** and **72** are layered on top of the other so that the orientation films **75** and **76** are made to face each other, and a homogeneous mixture containing a liquid crystal material, a polymerizable compound, a photopolymerization initiator, and a radical generating agent is injected between the substrates **71** and **72**.

Then, a photomask having a dot pattern as shown in Figure **43** is placed on one of the substrates **71** and **72**. Under this condition, the mixture is irradiated with UV-rays through the photomask. The photomask have masking portions corresponding to crossed regions of the electrode lines **73** and **74**. Because of this, the polymerizable compound is cured, and a phase separation occurred between the liquid crystal and the polymer. As a result, a display medium in which the liquid crystal regions **78** are partitioned by the polymer walls **77** is formed between the substrates **71** and **72**. The liquid crystal regions **78** are formed in regions corresponding to the masking portions. At this time, the size of the liquid crystal regions **78** can be regulated by adjusting the light-irradiated regions.

Then, the display medium is heated to thermally decompose the radical generating agent. Due to this, a radical is generated from the radical generating agent, and a remaining monomer before heating is polymerized by the radical, whereby the remaining monomer is decreased. Thus, the polymerization ratio is increased.

Thus, in the present example, the mixture injected between the facing substrates **71** and **72** is irradiated with UV-rays to obtain a display medium in which the liquid crystal regions **78** are dispersed in the polymer walls **77**. After that, the remaining monomer is polymerized by heating. Thus, the remaining monomer can be reduced. In the present example, the peeling between the substrates **71** and **72** and the polymer dispersed liquid crystal material, which is considered to be caused by the remaining monomer can be prevented. Moreover, the response speed and hysteresis can be improved.

It is preferred that the percentage of the remaining monomer (remaining monomer ratio Z) is 10% or less. More preferably, the ratio is in the range of 0.5% to 5%. Here, the remaining monomer ratio Z is calculated by the following equation:

$$\text{Remaining monomer ratio } Z = (X/X_0) \times 100$$

where X is a ratio of the light absorption of  $>C=C<$  (in the vicinity of 800 and 1600  $\text{cm}^{-1}$ ) in the photopolymerizable material and the light absorption of a carbonyl group (in the vicinity of 1700  $\text{cm}^{-1}$ ) of an ester in an infrared absorption spectrum of the polymer material obtained by excluding the liquid crystal material from the polymer dispersed liquid crystal material; and  $X_0$  is a ratio of the light absorption of  $>C=C<$  (in the vicinity of 800 and 1600  $\text{cm}^{-1}$ ) in the photopolymerizable material and the light absorption of a carbonyl group (in the vicinity of 1700  $\text{cm}^{-1}$ ) of an ester before the polymerization in an infrared absorption spectrum of the polymer material obtained by excluding the liquid crystal material from the polymer dispersed liquid crystal material.

The photopolymerizable material which is generally used is acrylate or methacrylate derivatives. In the above equation,  $X_0$  is almost constant, so that  $X_0 = 3$  is used in the present example.

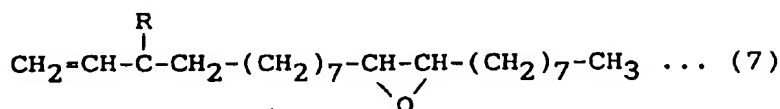
The reason why the remaining monomer ratio Z should be 10% or less is as follows:

When a polymer dispersed liquid crystal display device is manufactured only by general photopolymerization, the remaining monomer ratio exceeds 10%. When a great amount of multifunctional monomer is used, a network structure of the polymer material develops to increase the amount of monomer remaining in the network structure and the amount of contracted polymer material. Thus, the peeling and the like are caused between the substrate and the polymer dispersed liquid crystal material. In contrast, when the remaining monomer ratio is less than 0.5%, peroxides used in the present example should be added in a great amount. As a result, there is a possibility that the liquid crystal material is deteriorated, decreasing reliability.

Hereinafter, materials and the like applicable to the present example will be described.

(A liquid crystal material)

The liquid crystal material described: A liquid crystal material of Example 2 can be used. More preferred examples include compounds having a photopolymerizable group such as a methacrylate group or an acrylate group and a thermosetting group such as an isocyanate group or an epoxy group. Specific examples include 2-isocyanateethyl acrylate, 2-isocyanateethyl methacrylate, and a compound represented by the following Formula (7):



(A polymerizable liquid crystalline material)

5 The liquid crystal material described: A polymerizable liquid crystalline compound of Example 11 can be used.

The polymerizable liquid crystalline material is added for the purpose of making clear the phase separation and increasing response speed. Examples of the polymerizable liquid crystalline material include compounds having in its molecule a polymerizable functional group such as an acrylate group and a methacrylate group and a rigid functional group exhibiting liquid crystallinity.

10 It is preferred in terms of compatibility that the liquid crystal material and the liquid crystalline compound having a polymerizable functional group in its molecule are selected so that the respective portions of the liquid crystal material and the liquid polymerizable crystalline compound, exhibiting liquid crystallinity are similar to each other. In particular, in the case of liquid crystal materials of a fluorine type and/or a chlorine type which have specific chemical environment, it is preferred to select a liquid crystalline compound having a polymer-  
15 izable functional group of a fluorine type and/or a chlorine type.

In the case where ferroelectric liquid crystal is used, it is preferred to use a polymerizable compound having ferroelectric liquid crystal in its molecule in order to form a stable smectic phase.

Regarding the weight ratio of a compound having liquid crystallinity and a polymerizable non-liquid crystalline compound, it is preferred that the percentage of the compound having liquid crystallinity is 0.5% or more.  
20 In particular, in the case where ferroelectric liquid crystal is used, two regions (i.e., low molecular liquid crystal regions and polymer liquid crystal regions) are formed by making the amount of compound having liquid crystallinity 100%. Moreover, a voltage is used so as to drive the respective compounds (i.e., low molecular liquid crystal and polymer liquid crystal regions). In this way, a ferroelectric liquid crystal display device capable of performing a tone display can be manufactured.

25 (Weight ratio of liquid crystal and a polymerizable compound)

Same as that of Example 11.

30 (Structure of a polymer dispersed liquid crystal display device)

A structure in which a liquid crystalline compound (polymer) is fixed on polymer walls is preferred for making clear the phase separation and increasing the response speed. Due to this structure, the interfaces between the liquid crystalline and the polymer walls are driven by the application of a voltage. Under no applied  
35 voltage, the interaction between the liquid crystalline polymer and the polymer walls is increased, since the liquid crystal and the liquid crystalline polymer are bonded to each other. Thus, the response speed ( $\tau_r$ ) under an applied voltage and the response speed ( $\tau_d$ ) under no applied voltage can be improved. In the case of ferroelectric liquid crystal, because of the regulating ability of vertical polymer walls as well as the regulating ability of the substrate subjected to an orientation treatment, the orientation state is stabilized and shock resistance  
40 is improved. Moreover, a charge holding type element such as a TFT can be applied to the device without decreasing the electrical holding ratio of the entire device by using liquid crystal molecules having fluorine and/or chlorine atom(s) in their molecules, because the liquid crystal molecules have chemical stability.

(A photopolymerization initiator or a catalyst)

45 As a photopolymerization initiator, Irgacure 184, Irgacure 651, Irgacure 907, Darocure 1173, Darocure 1116, Darocure 2959, etc. can be used. The amount of the photopolymerization initiator is preferably in the range of 0.3% to 5% based on the total amount of the liquid crystal and the polymerizable compound. When the amount is less than 0.3%, sufficient photopolymerization reaction is not conducted; and when the amount  
50 is more than 5%, the phase separation between the liquid crystal and the polymer is conducted too fast to be regulated, forming smaller liquid crystal regions and increasing the drive voltage.

(A radical generating agent)

55 The radical generating agent generates a radical by being heated. Examples of the radical generating agent include peroxides having a -O-O- bond in molecules such as BPO, t-butyl peroxide, and lauryl peroxide; and azo compound liquid crystal having a -N=N- bond in molecules such as azobis(isobutyronitrile) (AIBN). It is preferred that the radical generating agent is added in an amount of 0.1 to 10% to the mixture of the photopolymerizable material and the photopolymerization initiator. When the added amount of the radical generating

agent is less than 0.1%, little effects of curing the remaining monomer after being irradiated with light are obtained; and when the added amount thereof is more than 10%, damage to the liquid crystal material is great, decreasing reliability.

5 The present example is applied to a non light scattering type; however, the present example is not limited thereto and can be applied to a light scattering type. Figure 46 shows a liquid crystal display device of a light scattering type. In this liquid crystal display device, two substrates 131 and 132 having electrode lines 133 and 134, respectively are made to face each other. Between the substrates 131 and 132, a plurality of liquid crystal droplets 137 are dispersed in the polymer walls 138. The liquid crystal droplets 137 are randomly dis-

10 posed, each of the droplets 137 having nonuniform size.

Hereinafter, the present example will be described by way of illustrating Applications.

#### Application 36

15 First, two flint glasses (manufactured by Nippon Sheet Glass Co., Ltd.) having ITO (a mixture of indium oxide and tin oxide) for electrodes with a thickness of 500 Angstroms were prepared as a substrate with a thickness of 1.1 mm. Then, the two flint glasses were disposed so that the respective ITO surfaces faced each other with spacers with a diameter of 12  $\mu\text{m}$  sandwiched therebetween. Thus, a cell was formed.

20 Next, a mixture for a display medium was injected into the cell. The mixture homogeneously contained 0.2 g of (R-684, manufactured by Nippon Kayaku K.K.), 0.35 g of 2-ethylhexyl acrylate, 0.45 g of isobornyl acrylate, 4 g of a liquid crystal material (ZLI-4792, manufactured by Merck & Co., Inc.), 0.05 g of a photopolymerization initiator (Irgacure 184), and 0.05 g of lauroyl oxide (laurox, manufactured by Kayaku Akuzo Co., Ltd.) as a radical generating agent (e.g., peroxide).

25 Next, the cell thus obtained was irradiated with UV-rays at 40 mW/cm<sup>2</sup> for one minute by using a high-pressure mercury lamp, whereby the polymerizable compound was cured.

Finally, the cell was allowed to stand in an atmosphere, for example, at 60°C for 50 hours, whereby a heat treatment was conducted. In this way, a liquid crystal display device of the present invention was manufactured.

#### Comparative Example 35

30 A cell was formed in the same way as in Application 36, and a polymer dispersed liquid crystal display device was manufactured by using a material obtained by excluding the radical generating agent from the mixture used in Application 36.

35 Table 22 shows electro-optic characteristics and a remaining polymer ratio of the liquid crystal display device of Application 36, before and after the heat treatment, together with a peeling state of the cell after the heat treatment. Table 22 also shows the results of Comparative Example 35 formed by heat treatment at 80°C for 4 hours. The electro-optic characteristics include a drive voltage, hysteresis, response speed, and an electrical holding ratio. The drive voltage is a voltage value at which a transmittance change is saturated. The hysteresis is the difference between the voltage in the case where transmittance is changed by 50% while the voltage increases and the voltage in the case where transmittance is changed by 50% while the voltage decreases. The response speed is the total time required for the transmittance to be changed by 90% (i.e., a sum of a time required when the transmittance is changed by 90% while voltage increases and a time required when the transmittance is changed by 90% while voltage decreases). The electrical holding ratio is the ratio of charge retained for 16.5 ms. In the item for the Peeling state, a mark ○ shows no change after the heat treatment; and a mark × shows that peeling has occurred in the vicinity of the seal. Moreover, the remaining monomer ratio is measured as follows:

45 One substrate of the cell is peeled off from the other substrate. The polymer dispersed liquid crystal material on the substrate is peeled off and mixed with KBr. Then, the mixture is measured, based on an infrared absorption spectrum.



Table 22

	Application 36		Comparative Example 35	
	Before heat treatment	After heat treatment	Before heat treatment	After heat treatment
Drive voltage (V)	12	12	12	12
Hysteresis (V)	0.3	0.1	0.3	0.3
Response speed (ms)	95	38	98	92
Electrical holding ratio (%)	97	97	97	97
Remaining monomer ratio (%)	13	4	14	14
Peeling state	-	○	-	×

As is understood from Table 22, in the case of Application 36, the drive voltage and the electrical holding ratio are almost the same as those of a conventional liquid crystal display device (Comparative Example 35). The hysteresis, response speed, remaining monomer ratio, and peeling state are improved, compared with the conventional prepared liquid crystal display device.

#### Application 37

First, as shown in Figure 35, two substrates 71 and 72 were prepared. In the respective substrates 71 and 72, electrode lines 73 and 74 were formed on a PET film with a thickness of 100  $\mu\text{m}$ . The electrode lines 73 and 74 were disposed with an interval of 50  $\mu\text{m}$  between lines, and each side length of the electrode lines 73 and 74 were 200  $\mu\text{m}$ . The number of the electrode lines 73 and 74 was 20. Then, a polyimide film was formed on the respective substrates 71 and 72 using SE150 (manufactured by Nissan Chemical Industries Ltd.) as orientation films 75 and 76, and the polyimide films were subjected to a rubbing treatment in one direction by using a nylon cloth.

Then, the two substrates 71 and 72 subjected to the rubbing treatment were made to face each other so that the respective electrode lines 73 and 74 crossed each other at right angles with spacers having a diameter of 6  $\mu\text{m}$  sandwiched therebetween. Thus, a cell was formed.

The photomask shown in Figure 43 was placed on the cell so that the masking portions 111 of the photomask covered the pixels, and a mixture was injected into the cell. The mixture homogeneously contained 0.1 g of trimethylol propane trimethacrylate, 0.35 g of 2-ethylhexyl acrylate, 0.45 g of isobornyl acrylate, 4 g of a liquid crystal material (ZLI-4792, manufactured by Merck & Co., Inc.) to which 0.3% of cholesteric nanonate (CN) was added, 0.05 g of a photopolymerization initiator (Irgacure 184), and 0.05 g of a radical generating agent (e.g., peroxide).

The cell thus obtained was irradiated through the photomask with UV-rays at 10 mW/cm<sup>2</sup> (the intensity of UV-rays measured at 365 nm) for 5 minutes by using a high-pressure mercury lamp which can provide parallel rays, whereby the polymerizable compound was cured. After that, the cell was heat-treated at 60°C for 10 hours.

One substrate of another cell formed in the same way as the above was peeled off from the other substrate. Then, the liquid crystal material was washed away from the substrate with acetone. A horizontal cross-section of the polymer walls on the substrate was observed by the SEM, revealing that liquid crystal regions with the same regularity as that of a dot pattern of the photomask (i.e., the same regularity as that of pixels) were uniformly formed, each liquid crystal region having almost the same size. Since some of the liquid crystal regions were damaged during the formation of the sample, 20 liquid crystal regions which had the most excellent regularity were selected for observation.

Finally, polarizing plates were attached to the cell so that the respective polarizing directions were aligned

with the orientation directions of the corresponding orientation films, whereby a polymer dispersed TN display device was manufactured.

#### 5 Comparative Example 36

A cell was formed by using glass with ITO having a thickness of, for example, 500 Angstroms (flint glass, manufactured by Nippon Sheet Glass Co., Ltd.) and using only the same liquid crystal material as that of Application 37. Polarizing plates were attached to the cell in the same way as in Application 37, whereby a conventional TN liquid crystal display device was manufactured.

#### 10 Comparative Example 37

A TN type cell was formed in the same way as in Application 37. Then, a mixture of the same liquid crystal as that of Application 37 and a photoreactive material excluding the polymerizable compound having a liquid crystalline functional group was injected into the cell, and the cell was irradiated with UV-rays in the same way as in Application 37 without using a photomask. Thus, a polymer dispersed liquid crystal display device was manufactured.

Table 23 shows the contrast and peeling state of the liquid crystal display device of Application 37 and those of Comparative Examples 36 and 37.

Table 23

	Application 37	Comparative	Comparative
Contrast	39	41	9
Peeling state	○	-	×

As is understood from Table 23, the liquid crystal display device of Application 37 had an electro-optic characteristic comparable to that of Comparative Example 36. Moreover, in Application 37, a film substrate can be used, and contrast is increased due to less light scattering in the pixels, compared with the conventional polymer dispersed liquid crystal display device (Comparative Example 37). Furthermore, in Application 37, almost no peeling occurred between the substrate and the polymer dispersed liquid crystal material.

#### 35 Application 38

First, two substrates subjected to a uniaxial orientation treatment in the same way as in Application 37 were made to face each other with silica beads having a diameter of 2  $\mu\text{m}$  sandwiched therebetween so that the respective rubbing directions were aligned. Thus, a cell was formed.

A mixture was injected into the cell thus obtained. The mixture homogeneously contained 0.01 g of trimethylol propane trimethacrylate, 0.025 g of lauryl acrylate, 0.025 g of isobornyl acrylate, 0.4 g of a ferroelectric liquid crystal material (ZLI-4003, manufactured by Merck & Co., Inc.), 0.05 g of a photopolymerization initiator (Irgacure 184), and 0.05 g of a radical generating agent (e.g., lauroyl peroxide).

Then, the photomask which was the same as that of Application 36 was placed on the cell. The cell was irradiated with UV-rays through the photomask at 10 mW/cm<sup>2</sup> (the intensity of UV-rays at 365 nm) for 5 minutes by using a high-pressure mercury lamp which can provide parallel rays, whereby the polymerizable compound was cured.

#### 50 Comparative Example 38

A cell was formed in the same way as in Application 38. Then, the ferroelectric liquid crystal (ZLI-4003) was injected into the cell, whereby a liquid crystal display device was manufactured.

#### 55 Comparative Example 39

A cell was formed in the same way as in Application 38. Then, the same mixture as that of Application 38 containing the liquid crystal and the photoreactive compound was injected into the cell. The cell was irradiated with UV-rays in the same way as in Application 36 without using a photomask, whereby a polymer dispersed

liquid crystal display device was manufactured.

Table 24 shows contrast and the results of an impact test of the liquid crystal display device of Application 38 and those of Comparative Examples 38 and 39. The impact test was conducted by dropping the cell from the height of 50 cm to rubber and inspecting the change in the orientation state. A mark ○ shows that the orientation is slightly disturbed in the boundary regions between the liquid crystal and the polymer causing no practical problems; and a mark × shows that the orientation was disturbed in the pixels. This shows problems for practical use.

Table 24

	Application 38	Comparative Example 38	Comparative Example 39
Contrast	38	40	8
Impact test	○	×	-

As is understood from Table 24, in Comparative Example 39, the liquid crystal molecules are not sufficiently aligned and contrast is low. As to the impact test, the liquid crystal display device of Comparative Example 39 cannot be evaluated since the liquid crystal molecules are not sufficiently aligned from the beginning. In Comparative Example 38, contrast is satisfactory, however, the result of the impact test is not good. In contrast, in Application 38, contrast is satisfactory and there is no problem with the orientation state in the impact test.

In Example 13, items described in Example 2: A light regulating means such as a photomask, Irradiation light, etc. can be applicable.

#### Example 14

Example 14 is the case where the phase separation between liquid crystal and a polymer is conducted without a photomask so that the liquid crystal and the polymer are not mixed with each other, and each liquid crystal region is disposed with respect to pixel(s).

Hereinafter, the present example will be described by way of illustrating Applications.

#### Application 39

A method for manufacturing a polymer dispersed liquid crystal display device including the step of irradiating light in a linear shape to each portion other than pixels will be described.

Figure 47 is a cross-sectional view showing one step of a method for manufacturing the polymer dispersed liquid crystal display device of Application 39. Figure 48 is a perspective view of the liquid crystal display device shown in Figure 47.

First, linear electrodes 142 formed of ITO (a mixture of indium oxide and tin oxide) were formed on two substrates 141. In Application 38, as the substrate 141, flint glass with a thickness of 1.1 mm and a side of 300 mm (manufactured by Nippon Sheet Glass Co., Ltd.) was used. The linear electrodes 142 had a thickness of 500 Angstroms and a width of 200 μm and were disposed with an interval of 50 μm therebetween. The number of the linear electrodes 142 on each substrate was 1000.

Next, polyimide (SE-150, manufactured by Nissan Chemical Industries Ltd.) was coated onto the substrates 141, on which the linear electrodes 142 were formed, by a spin coating method. The substrates 141 thus obtained were heat-treated to form orientation films. After that, the orientation films were subjected to a rubbing treatment in one direction by using a nylon cloth. Then, the two substrates 141 were made to face each other with spacers having a diameter of 6 μm sandwiched therebetween. At this time, the linear electrodes 142 on the respective substrates 141 crossed each other at right angles. Thus, a liquid crystal cell 144 was formed.

Next, a homogeneous mixture containing 0.1 g of trimethylol propane trimethacrylate, 0.4 g of 2-ethylhexyl acrylate and 0.5 g of isobornyl acrylate (as a photopolymerizable compound); 4 g of a mixture in which 0.3% of cholesteric nanonate was added to ZLI-3700-000 (manufactured by Merck & Co., Inc.) (as liquid crystal); and 0.1 g of Irgacure 184 (as a photopolymerization initiator) was injected into the liquid crystal cell 144. Crossed regions in which the linear electrodes 142 on the respective substrates 141 crossed each other with the mixture sandwiched therebetween became pixels 147.

Then, as shown in Figure 47, portions (i.e., non-pixel portions 145) excluding the pixels 147 were successively irradiated with a He-Cd laser beam as a linear light by a beam expander. As a result, the photopolymer-

izable compound in the mixture was cured to form polymer walls **148**.

As shown in Figure 48, the non-pixel portions **145** were formed of a plurality of non-pixel portions **145a** aligned in a vertical direction and a plurality of non-pixel portions **145b** aligned in a horizontal direction. First of all, as shown in Figure 48, the non-pixel portions **145a** (which were aligned in parallel in one direction) were successively irradiated with light from the end of the cell for 5 minutes each. Then, the non-pixel portions **145b** (which crossed the non-pixel portions **145a**) were successively irradiated with light for 5 minutes each in the same way. After that, a phase separation occurred between the liquid crystal and the polymer, whereby the polymer walls **148** were formed in the light-irradiated regions.

One substrate of the liquid crystal cell thus obtained was peeled off from the other substrate. Then, the liquid crystal material was washed away with acetone. A cross-section of the polymer walls **148** were observed by the SEM, revealing that the liquid crystal regions with the same regularity as that of the pixels were uniformly formed, each liquid crystal region having almost the same size, and the polymer walls with regularity were formed.

Polarizing plates were attached to the cell thus formed so that each polarizing direction was aligned with the orientation of the cell, whereby a polymer dispersed liquid crystal display device was obtained.

The transmittance of light passed through the liquid crystal display device under no voltage applied and the transmittance of light passed through the device under an applied 10 V voltage were measured. The ratio of the respective light transmittance, i.e., (light transmittance under an applied voltage)/(light transmittance under no applied voltage) was calculated to obtain contrast. The contrast of Application 39 was 38. When the liquid crystal display device was raised, non display irregularity was observed.

In Application 39, all of the non-pixel portions **145** were irradiated with light, whereby each liquid crystal region was formed in each pixel. However, the present invention is not limited thereto. If it is desired to form each liquid crystal region in a plurality of adjacent pixels **147**, the non-pixel portions **145** can partially be irradiated with light.

#### Application 40

A method for manufacturing a surface stabilized ferroelectric liquid crystal (SSFLC) display device including the step of irradiating light in a spot shape to each portion other than pixels. Figure 49 is a cross-sectional view showing one step of the method for manufacturing the surface stabilized ferroelectric liquid crystal (SSFLC) display device of Application 49. Figure 50 is a perspective view of the liquid crystal display device shown in Figure 49.

First, linear electrodes **142** formed of ITO with a thickness of 1000 Angstroms were formed on two substrates **141** by a wet etching method. Next, polyimide with a thickness of 500 Angstroms was coated onto the substrates **141**, on which the linear electrodes **142** were formed, by a spin coating method. The substrates **141** thus obtained were heated at 200°C for one hour to form orientation films. After that, the orientation films were subjected to a rubbing treatment in one direction. Then, the two substrates **141** were made to face each other with SiO beads having a diameter of 1.7  $\mu\text{m}$  sandwiched therebetween. At this time, the linear electrodes **142** on the respective substrates **141** faced and crossed each other at right angles, and the rubbing directions of the respective substrates **141** were aligned. Thus, a liquid crystal cell **144** was formed.

Next, a homogeneous mixture containing the same photopolymerizable compound as that of Application 39, a liquid crystal material (ZLI-4237-000, manufactured by Merck & Co., Inc.), and 0.1 g of a photopolymerization initiator (Irgacure 184) was injected into the liquid crystal cell **144**, under the condition that the mixture exhibited an isotropic liquid crystal phase at ordinary pressure.

Then, as shown in Figure 49, the cell was irradiated with a He-Cd laser beam, while non-pixel portions **145** were point-scanned. As shown in Figure 50, the non-pixel portions were formed of non-pixel portions **145c** in a dot shape.

First of all, as shown in Figure 50, the non-pixel portion **145c** situated at the end of the substrate **141** was irradiated with light in a spot shape, and then the other non-pixel portions **145c** were scanned at a speed of 1 mm/min. After that, the phase separation occurred between the liquid crystal and the polymer, whereby polymer walls **148** were formed in the light-irradiated regions.

Polarizing plates were attached to the cell in the same way as in Application 39 so that each polarizing direction was aligned with the orientation of the cell, whereby a liquid crystal display device was obtained.

In Application 40, all of the non-pixel portions **145** were irradiated with light, whereby each liquid crystal region is formed in each pixel. The present invention is not limited thereto. If it is desired that each liquid crystal region be formed in a plurality of adjacent pixels, the non-pixel portions **145** can partially be irradiated with light.

## Application 41

A method for manufacturing a surface stabilized ferroelectric liquid crystal (SSFLC) display device will be described. This method includes the steps of forming an insulating film on linear electrodes provided on one transparent substrate and irradiating light to a portion of a mixture which is not covered with the insulating film. Figure 51 is a cross-sectional view showing one step of the method for manufacturing the surface stabilized ferroelectric liquid crystal (SSFLC) display device of Application 41.

Linear electrodes 142 were formed on two substrates 141 in the same way as in Application 40. Then, an insulating film 146 (refractive index: 1.4) formed of OCD (manufactured by Tokyo Ohyo Kagaku Co., Ltd.) was formed only on the linear electrode 142 provided on one substrate 141. The refractive index of the linear electrode 142 was 1.5. Then, the same steps as those of Application 40 were used to form a liquid crystal cell 144. The same mixture as that of Application 40 was injected into the cell.

Next, as shown in Figure 51, parallel rays (UV-rays) were irradiated through toluene in a container 149 to the substrate 141 on which the insulating film 146 was formed at an incident angle of 80°. In this case, since light was passed through non-pixel portions 145, the photopolymerizable compound contained in the mixture was cured. In pixels 147, a double structure including the linear electrode 142 and the insulating film 146 was formed, so that light was reflected from the interface between the linear electrode 142 and the insulating film 146. Thus, in the pixels 147, a photosetting reaction was not conducted. Because of this, the photopolymerizable compound was selectively cured with regularity, and phase separation occurred between the liquid crystal and the polymer, whereby polymer walls 148 were formed only in the non-pixel portions 145. In application 41, the cell was irradiated with UV-rays at 10 mW/cm<sup>2</sup> for 10 minutes by using a high-pressure mercury lamp which can provide parallel rays.

Polarizing plates were attached to the cell in the same way as in Application 39, whereby a liquid crystal display device was obtained.

Tables 25 and 26 show the results obtained by measuring shock resistance, using the liquid crystal display devices of Applications 40 and 41. The disturbance of the liquid crystal molecules orientation was checked in a pressure test by applying a load of 5 kgf/cm<sup>2</sup> at a speed of 0.5 mm/min and in a drop test by allowing the cell to drop by its own weight from a height of 5 cm to a floor.

Table 25

Results of a pressure test	
	Evaluation
Application 40	Partial disturbance of the orientation was found in the entire region to which a pressure was applied.
Application 41	Partial disturbance of the orientation was found in the entire region to which a pressure was applied.

Table 26

Drop test	
	Evaluation
Application 40	No disturbance of the orientation was found.
Application 41	No disturbance of the orientation was found.

As is understood from Tables 25 and 26, the liquid crystal display devices of Applications 40 and 41 have satisfactory durability of their liquid crystal, and the cell thickness can be maintained with precision.

Hereinafter, materials and the like applicable to the present example will be described.

(An optical source used for light irradiation)

In the case of irradiating light over the entire surface of the substrate, a mercury lamp is used. In the case of irradiating light to part of the surface of the substrate, a He-Cd laser, an excimer laser, and a dye laser can

be used.

The materials described: A polymer material, A liquid crystal material, and A photopolymerization initiator in Example 2 can be used in the present example.

Various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the scope and spirit of this invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the description as set forth herein, but rather that the claims be broadly construed.

## Claims

1. A liquid crystal display device comprising:
  - two substrates facing each other, at least one of the substrates being transparent;
  - electrodes disposed on inside surfaces of the respective substrates;
  - a display medium which is provided between the two substrates and formed of polymer walls and liquid crystal regions partitioned by the polymer walls; and
  - a plurality of pixels,
  - wherein an interval  $a$  between a center of one liquid crystal region and a center of an adjacent liquid crystal region in a direction along a surface of the substrate is within a width of one pixel along the direction, and 80% or more of the intervals  $a$  satisfy the relationship:  $3b/2 > a > b/2$ , where  $b$  is an average of the intervals  $a$ .
2. A method for manufacturing a liquid crystal display device having a plurality of pixels, comprising the steps of:
  - providing a mixture containing a photopolymerizable compound and a liquid crystal material between a pair of substrates, two substrates facing each other, at least one of the substrates being transparent, electrodes being disposed on inside surfaces of the respective substrates; and
  - irradiating light to the mixture with a light intensity distribution in which light intensity of at least one portion of each pixel is 90% or less of a maximum illuminance in a circular area which corresponds to 10 times the pixel area and whose center is situated in a center of the pixel.
3. A method for manufacturing a liquid crystal display device according to claim 2, wherein a photomask having a pattern with regularity is placed on the transparent substrate, and light is irradiated through the photomask to the mixture provided between the substrates.
4. A method for manufacturing a liquid crystal display device according to claim 3, wherein the pattern with regularity is formed on the photomask, and the pattern covers 30% or more of at least each pixel.
5. A method for manufacturing a liquid crystal display device according to claim 3, wherein the pattern with regularity is formed on the photomask, a minimum repeating unit of the pattern has a size within a circle having a diameter in the range of  $1\text{ }\mu\text{m}$  to  $50\text{ }\mu\text{m}$ , and an interval between a center of one unit and a center of an adjacent unit is in the range of  $1\text{ }\mu\text{m}$  to  $50\text{ }\mu\text{m}$ .
6. A method for manufacturing a liquid crystal display device according to claim 2, wherein the photomask having a pattern with regularity is placed inside one of the substrates, and light is irradiated through the photomask to the mixture provided between the substrates.
7. A method for manufacturing a liquid crystal display device according to claim 6, wherein the pattern with regularity is formed on the photomask, and the pattern covers 30% or more of at least each pixel.
8. A method for manufacturing a liquid crystal display device according to claim 7, wherein the pattern with regularity is formed on the photomask, a minimum repeating unit of the pattern has a size within a circle having a diameter in the range of  $1\text{ }\mu\text{m}$  to  $50\text{ }\mu\text{m}$ , and an interval between a center of one unit and a center of an adjacent unit is in the range of  $1\text{ }\mu\text{m}$  to  $50\text{ }\mu\text{m}$ .
9. A liquid crystal display device comprising:
  - two substrates facing each other, at least one of the substrates being transparent, electrodes disposed on inside surfaces of the respective substrates; and
  - a display medium which is provided between the two substrates and formed of polymer walls con-

taining a polymer as their main component and liquid crystal regions containing liquid crystal as their main component;

wherein the liquid crystal regions are partitioned by the polymer walls and are close to the substrates, portions of the liquid crystal regions close to the substrates being in parallel with the substrates.

10. A liquid crystal display device according to claim 9, wherein an orientation direction of a plurality of liquid crystal molecules contained in each of the liquid crystal regions is concentric along the polymer walls within a plane which is in parallel with the substrates.
11. A liquid crystal display device according to claim 9, wherein each of the liquid crystal regions has a plurality of liquid crystal domains and an orientation direction of each of the liquid crystal domains is concentric along the polymer walls within a plane which is in parallel with the substrates.
12. A liquid crystal display device according to claim 9, wherein each of the liquid crystal regions has an inside liquid crystal domain situated in a center thereof, a polymer region surrounding an outside of the inside liquid crystal domain, and a plurality of outside liquid crystal domains surrounding an outside of the polymer region; and the respective outside liquid crystal domains are aligned in a radial manner within a plane which is in parallel with the substrates.
13. A liquid crystal display device according to claim 9, wherein the liquid crystal regions have a plurality of liquid crystal domains, and an orientation direction of each of the liquid crystal domains is different within a plane which is in parallel with the substrates.
14. A liquid crystal display device according to claim 9, wherein the liquid crystal regions have a polymer region positioned in the center thereof and a plurality of liquid crystal domains surrounding an outside of the polymer region, and the respective liquid crystal domains are aligned in a radial manner within a plane which is in parallel with the substrates.
15. A liquid crystal display device according to claim 9, comprising a plurality of pixels, wherein the liquid crystal regions are provided in at least one pixel.
16. A liquid crystal display device according to claim 15, wherein at least one liquid crystal region contained in the pixel has a size of 30% or more of the pixel size.
17. A liquid crystal display device according to claim 15, wherein an orientation direction of a plurality of liquid crystal molecules contained in each of the liquid crystal regions is concentric along the polymer walls within a plane which is in parallel with the substrates.
18. A liquid crystal display device according to claim 15, wherein each of the liquid crystal regions has a plurality of liquid crystal domains, and an orientation direction of each of the liquid crystal domains is concentric along the polymer walls within a plane which is in parallel with the substrates.
19. A liquid crystal display device according to claim 15, wherein the liquid crystal regions have an inside liquid crystal domain positioned in a center thereof, a polymer region surrounding an outside of the inside liquid crystal domain, and a plurality of outside liquid crystal domains surrounding an outside of the polymer region; and the respective outside liquid crystal domains are aligned in a radial manner within a plane which is in parallel with the substrates.
20. A liquid crystal display device according to claim 15, wherein the liquid crystal regions have a plurality of liquid crystal domains, and an orientation direction of each of the liquid crystal domains is different within a plane which is in parallel with the substrates.
21. A liquid crystal display device according to claim 15, wherein the liquid crystal regions have a polymer region positioned in a center thereof and a plurality of liquid crystal domains surrounding an outside of the polymer region; and the respective liquid crystal domains are aligned in a radial manner within a plane which is in parallel with the substrates.
22. A liquid crystal display device according to claim 9, comprising a plurality of pixels, wherein two or more of the liquid crystal regions are entirely or partially provided in one pixel.

23. A liquid crystal display device according to claim 22, wherein the pixel has a longitudinal side of 200  $\mu\text{m}$  or more.
- 5 24. A liquid crystal display device according to claim 22, wherein an orientation direction of a plurality of liquid crystal molecules contained in the liquid crystal regions are concentric along the polymer walls within a plane which is in parallel with the substrates.
- 10 25. A liquid crystal display device according to claim 22, wherein each of the liquid crystal regions has a plurality of liquid crystal domains, and an orientation direction of each of the liquid crystal domains is concentric along the polymer walls within a plane which is in parallel with the substrates.
- 15 26. A liquid crystal display device according to claim 22, wherein each of the liquid crystal domains has an inside liquid crystal domain positioned in a center thereof, a polymer region surrounding an outside of the inside liquid crystal domain, and a plurality of liquid crystal domains surrounding an outside of the polymer region; and the respective outside liquid crystal domains are aligned in a radial manner within a plane which is in parallel with the substrates.
- 20 27. A liquid crystal display device according to claim 22, wherein the liquid crystal region has a plurality of liquid crystal domains, and an orientation direction of each of the liquid crystal domains is different within a plane which is in parallel with the substrates.
- 25 28. A liquid crystal display device according to claim 22, wherein each of the liquid crystal regions has a polymer region positioned in a center thereof and a plurality of liquid crystal domains surrounding an outside of the polymer region, and the respective liquid crystal domains are aligned in a radial manner within a plane which is in parallel with the substrates.
- 30 29. A liquid crystal display device according to claim 9, wherein a plurality of liquid crystal molecules contained in each of the liquid crystal regions are aligned in a helical manner along a helical axis which is vertical with respect to the substrates.
- 35 30. A liquid crystal display device according to claim 29, wherein the plurality of liquid crystal molecules contained in each of the liquid crystal regions are provided with a helical pitch of 15  $\mu\text{m}$  to 100  $\mu\text{m}$ .
- 40 31. A liquid crystal display device according to claim 9, wherein  $d \times \Delta n$  is in the range of 0.4  $\mu\text{m}$  to 1.1  $\mu\text{m}$ ; and a distance between the substrates is in the range of 3  $\mu\text{m}$  to 10  $\mu\text{m}$ , where  $d$  is a thickness between horizontal portions in each of the liquid crystal regions and  $\Delta n$  is anisotropy of refractive index thereof.
- 45 32. A liquid crystal display device according to claim 9, wherein the display medium has a structure in which a liquid crystalline compound is fixed in the vicinity of an interface between the liquid crystal region and the polymer wall.
- 50 33. A liquid crystal display device according to claim 32, wherein anisotropy of dielectric constant  $\Delta\epsilon_L$  of the liquid crystal region and anisotropy of dielectric constant  $\Delta\epsilon_P$  of the liquid crystalline compound have a relationship of  $\Delta\epsilon_L \times \Delta\epsilon_P < 0$ .
- 55 34. A liquid crystal display device according to claim 32, wherein the liquid crystalline compound has at least one of a fluorine atom and a chlorine atom and the liquid crystal region is formed from a liquid crystal material having at least one of fluorine atom and a chlorine atom in its molecule.
35. A liquid crystal display device according to claim 34, wherein the liquid crystalline compound has an optically active group in its molecule and the liquid crystal region is formed from ferroelectric liquid crystal.
36. A liquid crystal display device according to claim 32, wherein the polymer walls are formed in a liquid crystal state.
37. A liquid crystal display device according to claim 36, wherein the liquid crystal regions and the polymer walls contain a dichroic dye.
38. A liquid crystal display device according to claim 32, wherein the polymer walls are formed in a liquid crystal state, and the polymer walls and the liquid crystal regions are in the same orientation when no voltage



is applied to the display medium.

- 5 39. A liquid crystal display device according to claim 38, wherein at least one of the substrates has an orientation film in contact with the display medium, and the polymer walls and the liquid crystal regions are in the same orientation, based on the orientation film.
40. A liquid crystal display device according to claim 39, wherein the liquid crystal regions and the polymer walls contain a dichroic dye.
- 10 41. A liquid crystal display device according to claim 9, wherein anisotropy of dielectric constant  $\Delta\epsilon_L$  of the liquid crystal region and anisotropy of dielectric constant  $\Delta\epsilon_P$  of the liquid crystalline compound have a relationship of  $\Delta\epsilon_L \times \Delta\epsilon_P < 0$ .
- 15 42. A liquid crystal display device according to claim 9, wherein a remaining monomer ratio obtained from infrared absorption caused by a double bond between carbons in the polymer wall and infrared absorption caused by a carbonyl group of an ester in the polymer wall is 10% or less.
- 20 43. A liquid crystal display device according to claim 9, wherein a light-intercepting mask is placed on one of the substrates so that light-intercepting portions of the mask cover portions where the substrate and the polymer walls are in contact with each other.
- 25 44. A liquid crystal display device according to claim 43, wherein the light-intercepting mask is placed so that the light-intercepting portions thereof cover 50% or more of the respective portions where the substrate and the polymer walls are in contact with each other.
- 30 45. A liquid crystal display device according to claim 9, wherein orientation films are respectively formed on the electrodes mounted on the substrates.
- 35 46. A liquid crystal display device according to claim 45, wherein the orientation films are uniaxially aligned by an orientation treatment.
- 40 47. A liquid crystal display device according to claim 45, wherein at least one of the orientation films contain a photopolymerization initiator.
- 45 48. A liquid crystal display device according to claim 9, wherein a polarizing plate is provided outside of at least one of the substrates.
- 50 49. A method for manufacturing a liquid crystal display device having a plurality of pixels, comprising the steps of:
  - 40 providing a mixture containing a photopolymerizable compound and a liquid crystal material between a pair of substrates, two substrates facing each other, at least one of the substrates being transparent, and electrodes being disposed on inside surfaces of the respective substrates, thereby forming a cell; and
  - 45 irradiating the mixture with light under the condition that intensity of light is reduced in predetermined portions of the mixture, thereby forming a display medium between the substrates, the display medium having polymer walls containing a polymer as their main component and liquid crystal regions containing liquid crystal as their main component.
- 55 50. A method for manufacturing a liquid crystal display device according to claim 49, wherein the predetermined portions correspond to at least one pixel, whereby the liquid crystal regions are provided in at least one pixel.
51. A method for manufacturing a liquid crystal display device according to claim 49, wherein an area of each of the predetermined portions corresponds to 30% or more of each pixel area, whereby at least one liquid crystal region contained in the pixel is made 30% or more of the pixel area.
52. A method for manufacturing a liquid crystal display device according to claim 49, wherein means for reducing intensity of light is a photomask, and the photomask is placed on the side of the display medium of one of the substrates.

53. A method for manufacturing a liquid crystal display device according to claim 49, wherein the mixture is irradiated with light through a photomask, the photomask having a plurality of masking portions for forming the liquid crystal regions and each of the masking portion having at least one light transmission hole at least in a center thereof, whereby liquid crystal domains are formed in a radial manner in each of the liquid crystal regions.
54. A method for manufacturing a liquid crystal display device according to claim 53, using a photomask having masking portions for forming the liquid crystal regions, each of the masking portions having a light transmission hole in a center thereof and light transmission slits disposed in a radial manner around the transmission hole.
55. A method for manufacturing a liquid crystal display device according to claim 49, wherein the mixture is irradiated with light while alternating a light-irradiating period and a non light-irradiating period.
56. A method for manufacturing a liquid crystal display device according to claim 49, wherein the mixture further contains a compound having effects for suppressing photopolymerization.
57. A method for manufacturing a liquid crystal display device according to claim 49, wherein the display medium having walls containing a polymer as their main component and liquid crystal regions containing liquid crystal as their main component is formed between the substrates by irradiating light to all of the portions or part thereof excluding the pixels.
58. A method for manufacturing a liquid crystal display device according to claim 57, wherein light which is irradiated to all of the portions or part thereof excluding the pixels is linear light.
59. A method for manufacturing a liquid crystal display device according to claim 57, wherein light irradiation to all of the portions or part thereof excluding the pixels is conducted while spot light in a dot shape is moved.
60. A method for manufacturing a liquid crystal display device according to claim 49, wherein means for reducing intensity of light is an insulating film formed on the electrode of one of the substrates, and the display medium having walls containing a polymer as its main component and liquid crystal regions containing liquid crystal as its main component is formed between the substrates by irradiating light to the mixture from the side of the substrate on which the insulating film is formed.
61. A method for manufacturing a liquid crystal display device according to claims 49, wherein the step of forming a cell is conducted by attaching the two substrates after providing the mixture on one of the substrates.
62. A method for manufacturing a liquid crystal display device according to claim 49, wherein polarizing plates are formed on external surfaces of the two substrates.
63. A method for manufacturing a liquid crystal display device having a plurality of pixels, comprising the steps of:  
     forming an orientation film containing a photopolymerization initiator on at least one of a pair of substrates, two substrates facing each other, at least one of the substrates being transparent, and electrodes being disposed on inside surfaces of the respective substrates;  
     subjecting the substrate on which the orientation film is formed to a rubbing treatment in one direction;  
     providing a mixture containing a photopolymerizable compound and a liquid crystal material between the pair of substrates after the rubbing treatment; and  
     forming a display medium having polymer walls containing a polymer as their main component and liquid crystal regions containing liquid crystal as their main component by curing the photopolymerizable compound.
64. A method for manufacturing a liquid crystal display device according to claim 63, wherein the photopolymerizable compound contained in the mixture contains a liquid crystalline compound having at least one polymerizable functional group in its molecule.
65. A method for manufacturing a liquid crystal display device according to claim 64, wherein a compound

having a polymerizable functional group, at least one of a fluorine atom and a chlorine atom in its molecule is used as the liquid crystalline compound, and a liquid crystal material having at least one of a fluorine and a chlorine atom in its molecule is used for the liquid crystal regions.

- 5 66. A method for manufacturing a liquid crystal display device according to claim 65, wherein a compound having a polymerizable functional group and an optically active group in its molecule is used as the liquid crystalline compound, and ferroelectric liquid crystal is used for the liquid crystal regions.
- 10 67. A method for manufacturing a liquid crystal display device according to claim 63, wherein UV-rays are irradiated to the mixture so that portions where the liquid crystal regions are to be formed become weak light-irradiated regions, thereby optically polymerizing the photopolymerizable compound.
- 15 68. A method for manufacturing a liquid crystal display device according to claim 67, wherein means for forming weak light-irradiated regions is a photomask, and the photomask is placed on the side of the display medium of one of the substrates.
- 20 69. A method for manufacturing a liquid crystal display device according to claims 63, wherein the step of forming a cell is conducted by attaching the two substrates after providing the mixture on one of the substrates.
- 25 70. A method for manufacturing a liquid crystal display device according to claim 63, wherein polarizing plates are formed on external surfaces of the two substrates.
- 30 71. A method for manufacturing a liquid crystal display device having a plurality of pixels, comprising the steps of:
  - forming a thin film pattern containing a photopolymerization initiator on one surface of at least one of a pair of substrates, the substrates respectively having electrodes and at least one of the substrates being transparent;
  - providing a mixture containing a polymerizable compound and a liquid crystal material between the pair of substrates, at least one of the substrates having the thin film pattern, thereby forming a cell; and
  - forming a display medium between the substrates by curing the polymerizable compound, the display medium having polymer walls containing a polymer as their main component and liquid crystal regions containing liquid crystal as their main component.
- 35 72. A method for manufacturing a liquid crystal display device according to claim 71, wherein the polymerization initiator is a photopolymerization initiator, the polymerizable compound is a photopolymerizable compound, a photomask allowing 50% or more of the thin film pattern to be exposed is placed outside of one of the substrates, and light is irradiated to the photopolymerizable initiator and the photopolymerizable compound through the photomask to cure the photopolymerizable compound.
- 40 73. A method for manufacturing a liquid crystal display device according to claim 72, wherein the photopolymerizable compound contained in the mixture contains a liquid crystalline compound having at least one kind of polymerizable functional group at its molecule.
- 45 74. A method for manufacturing a liquid crystal display medium according to claim 73, wherein a compound having a polymerizable functional group, and at least one of a fluorine atom and a chlorine atom in its molecule is used as the liquid crystalline compound; and a liquid crystal material having at least one of a fluorine atom and a chlorine atom in its molecule is used for the liquid crystal regions.
- 50 75. A method for manufacturing a liquid crystal display device according to claim 73, wherein a compound having a polymerizable functional group and an optically active group in its molecule is used as the liquid crystalline compound and ferroelectric liquid crystal is used for the liquid crystal regions.
- 55 76. A method for manufacturing a liquid crystal display device according to claim 71, wherein UV-rays are irradiated to the mixture so that portions where the liquid crystal regions are to be formed become weak light-irradiated regions, thereby optically polymerizing the polymerizable compound.
77. A method for manufacturing a liquid crystal display device according to claim 71, wherein the polymerization initiator is a heat polymerization initiator, the polymerizable compound is a heat polymerizable compound, and the heat polymerization initiator and the mixture are heated to cure the heat polymerizable

compound.

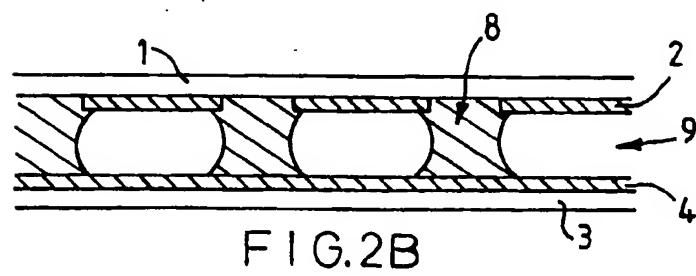
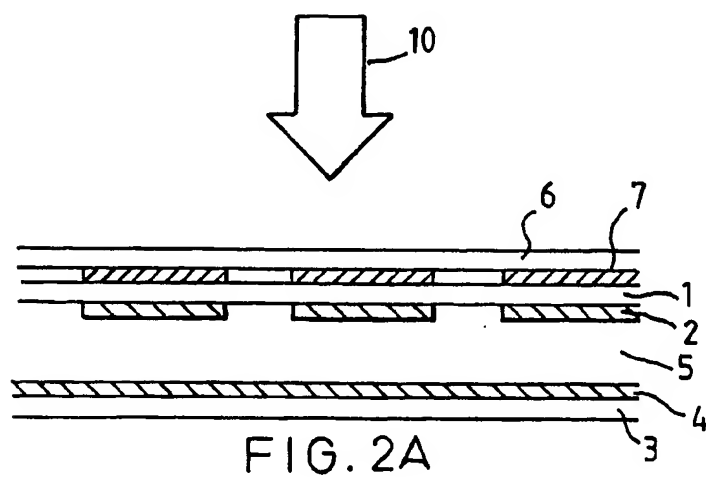
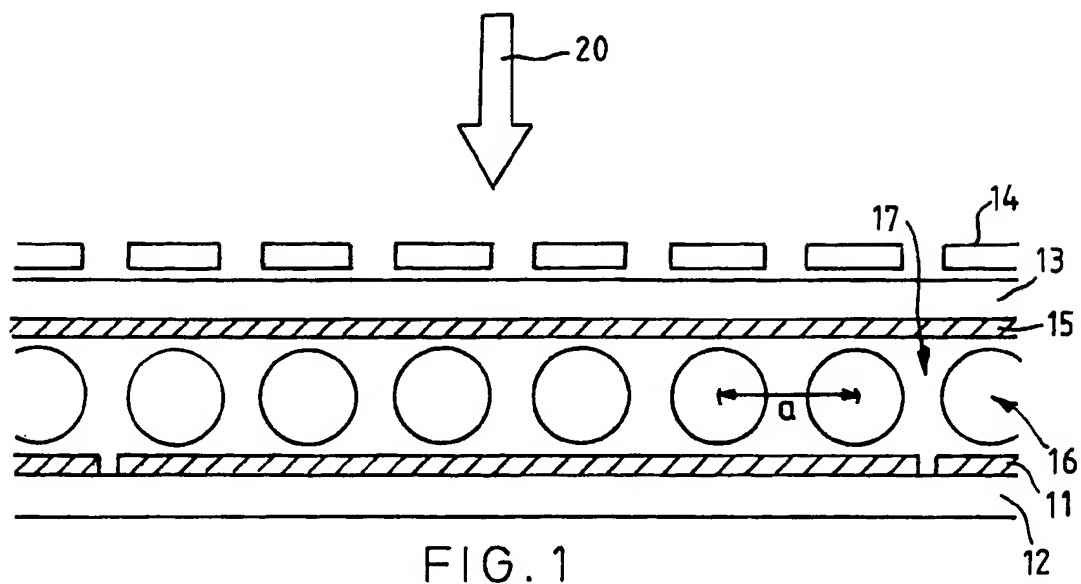
- 5 78. A method for manufacturing a liquid crystal display device according to claims 71, wherein the step of forming a cell is conducted by attaching the two substrates after providing the mixture on one of the substrates.
79. A method for manufacturing a liquid crystal display device according to claim 71, wherein polarizing plates are formed on external surfaces of the two substrates.
- 10 80. A method for manufacturing a liquid crystal display device having a plurality of pixels, comprising the steps of:
  - 15 providing a mixture between a pair of substrates facing each other, thereby forming a cell, at least one of the substrates being transparent, electrodes being disposed on inside surfaces on the respective substrates, the mixture containing a liquid crystal material, a polymerizable liquid crystalline material having a liquid crystalline functional group in its molecule, a polymerizable compound, and a polymerization initiator, anisotropy of dielectric constant  $\Delta\epsilon_L$  of the liquid crystal material and anisotropy of dielectric constant  $\Delta\epsilon_P$  of the polymerizable liquid crystalline material having a relationship of  $\Delta\epsilon_L \times \Delta\epsilon_P < 0$ , and
  - 20 forming a display medium between the substrates by polymerizing the polymerizable compound, the display medium having polymer walls containing a polymer as their main component and liquid crystal regions containing liquid crystal as their main component, providing the liquid crystalline functional groups in the liquid crystal regions to fix a liquid crystalline polymer on the polymer walls.
81. A method for manufacturing a liquid crystal display device according to claim 80, wherein the polymerizable compound is a photopolymerizable compound, the polymerization initiator is a photopolymerization initiator, and the polymerizable compound is optically polymerized.
82. A method for manufacturing a liquid crystal display device according to claim 81, wherein UV-rays are irradiated to the mixture so that portions where the liquid crystal regions are to be formed become weak light-irradiated regions, thereby optically polymerizing the mixture.
- 30 83. A method for manufacturing a liquid crystal display device according to claim 82, wherein means for forming the weak light-irradiated regions is a photomask, and the photomask is placed on the side of the display medium of one of the substrates.
- 35 84. A method for manufacturing a liquid crystal display device according to claim 80, wherein the polymerizable compound is a heat polymerizable compound, the polymerization initiator is a heat polymerization initiator, and the polymerizable compound is polymerized by heating.
- 40 85. A method for manufacturing a liquid crystal display device according to claim 80, wherein a compound having at least one of a fluorine atom and a chlorine atom in its molecule is used as the liquid crystal material and the polymerizable liquid crystalline material.
- 45 86. A method for manufacturing a liquid crystal display device according to claims 80, wherein the step of forming a cell is conducted by attaching the two substrates after providing the mixture on one of the substrates.
87. A method for manufacturing a liquid crystal display device according to claim 80, wherein the step of forming a cell comprises the steps of:
  - 50 coating the mixture onto one of the substrates, the mixture further containing a solvent capable of homogeneously dissolving the liquid crystal material and the polymerizable liquid crystalline material;
  - removing the solvent from the mixture coated onto one of the substrates by evaporation to provide the liquid crystalline functional groups in the liquid crystal regions, thereby fixing a liquid crystalline compound on the polymer walls; and
  - placing the other substrate on the substrate on which the mixture is coated.
- 55 88. A method for manufacturing a liquid crystal display device according to claim 80, wherein polarizing plates are formed on external surfaces of the two substrates.
89. A method for manufacturing a liquid crystal display device having a plurality of pixels, comprising the steps of:

providing a mixture between a pair of substrates facing each other, thereby forming a cell, at least one of the substrates being transparent, electrodes being disposed on inside surfaces of the respective substrates, the mixture containing a liquid crystal material, a photopolymerizable compound, a photopolymerization initiator, and a radical generating agent;

irradiating light to the mixture to cause a phase separation, thereby obtaining a state in which liquid crystal regions are dispersed in the polymer walls; and

thermally decomposing the radical generating agent by heating the display medium.

90. A method for manufacturing a liquid crystal display device according to claim 89, wherein UV-rays are irradiated to the mixture so that portions where the liquid crystal regions are to be formed become weak light-irradiated regions, thereby optically polymerizing the polymerizable compound.
91. A method for manufacturing a liquid crystal display device according to claim 90, wherein means for forming the weak light-irradiated regions is a photomask, and the photomask is placed on the side of the display medium of one of the substrates.
92. A method for manufacturing a liquid crystal display device according to claim 89, wherein a liquid crystal material of at least one of a fluorine type and chlorine type is used as the liquid crystal material.
93. A method for manufacturing a liquid crystal display device according to claim 89, wherein the photopolymerizable compound contains a photopolymerizable liquid crystal compound.
94. A method for manufacturing a liquid crystal display device according to claims 89, wherein the step of forming a cell is conducted by attaching the two substrates after providing the mixture on one of the substrates.
95. A method for manufacturing a liquid crystal display device according to claim 89, wherein polarizing plates are formed on external surfaces of the two substrates.



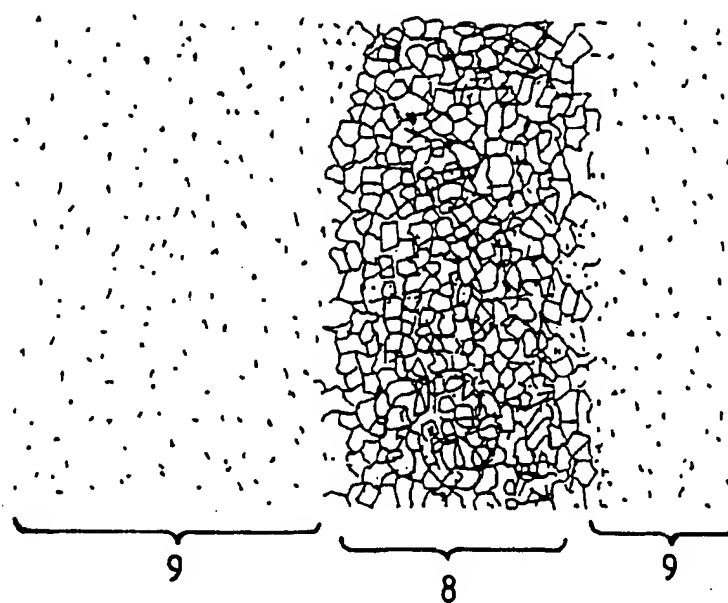


FIG. 3

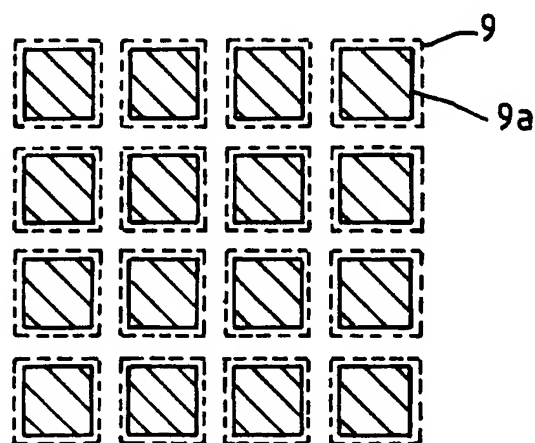


FIG. 4

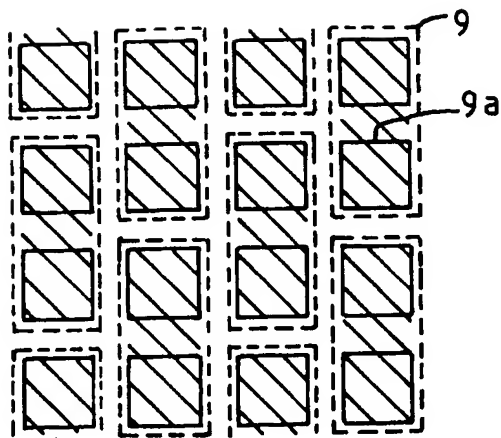


FIG. 5A

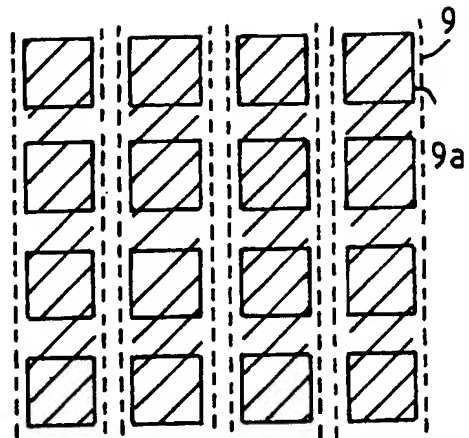


FIG. 5b

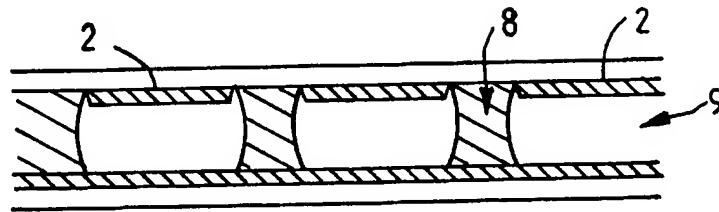


FIG. 6

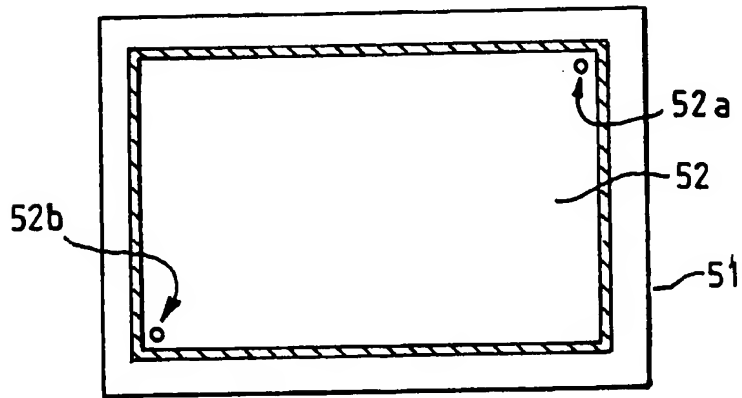


FIG 7

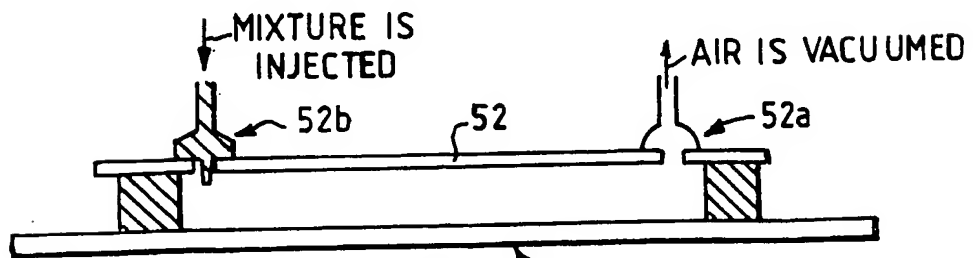


FIG. 8



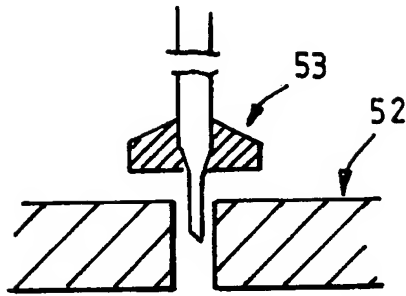


FIG. 9

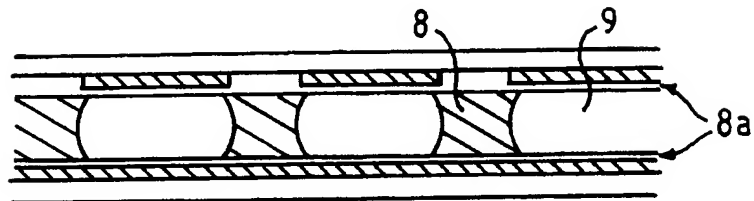


FIG. 10A

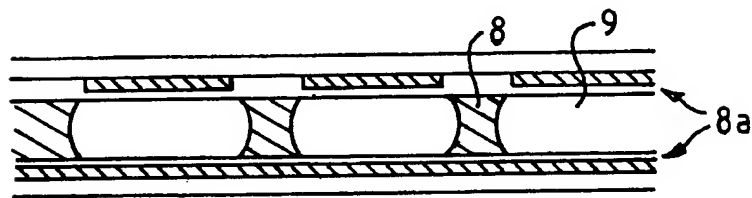


FIG. 10B

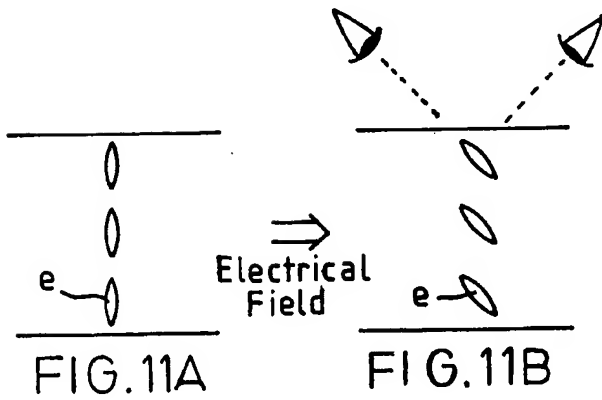


FIG. 11A

FIG. 11B

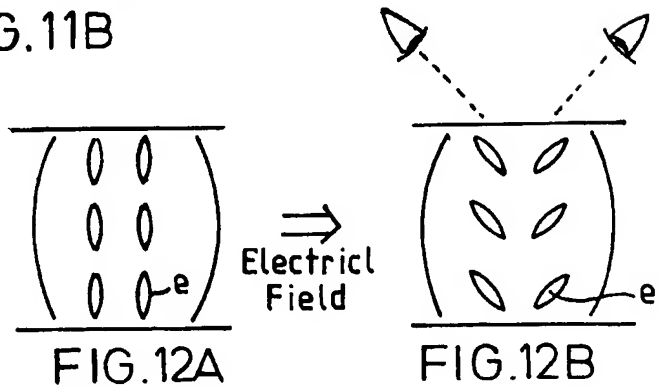


FIG. 12A

FIG. 12B

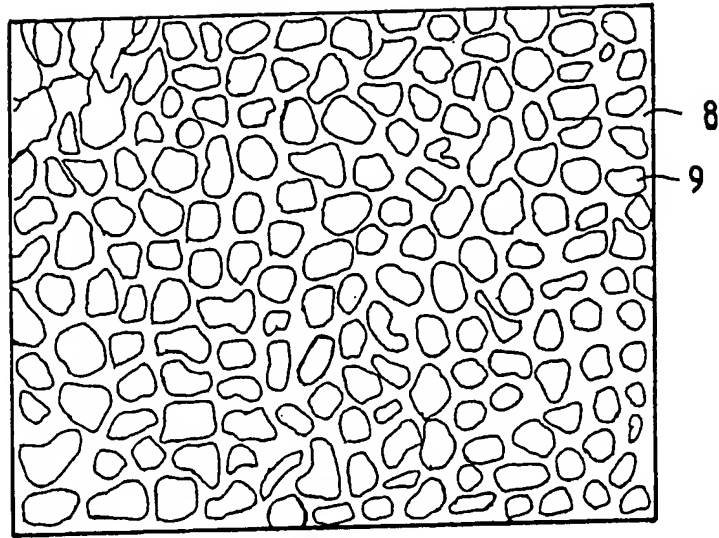


FIG.13

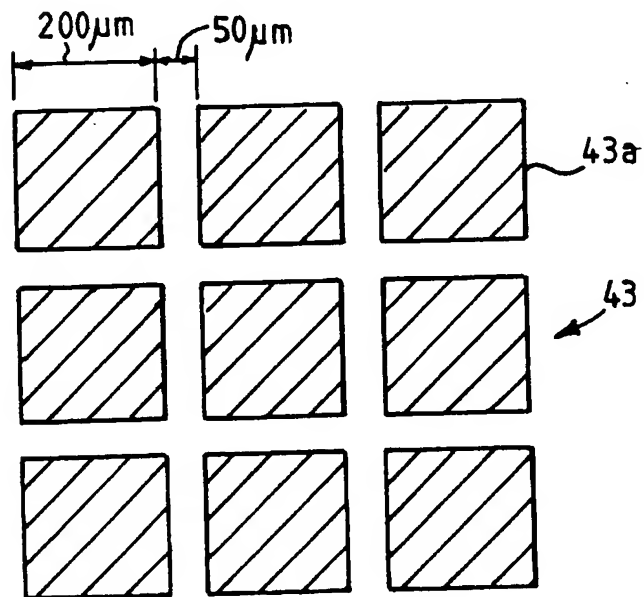


FIG.14

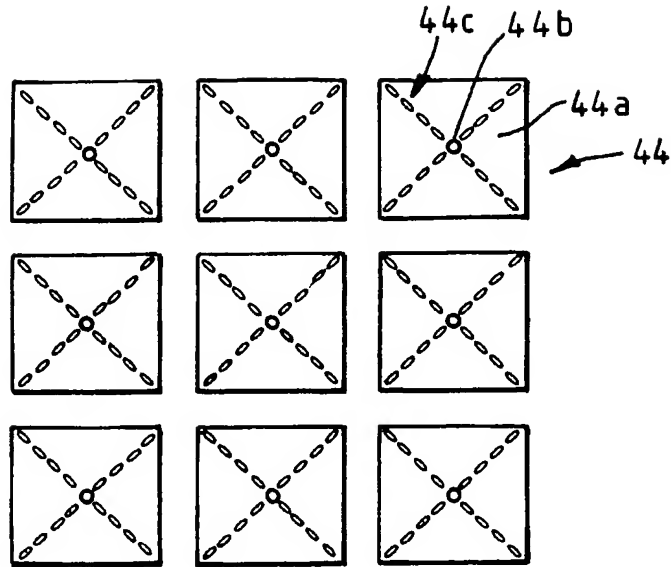


FIG. 15

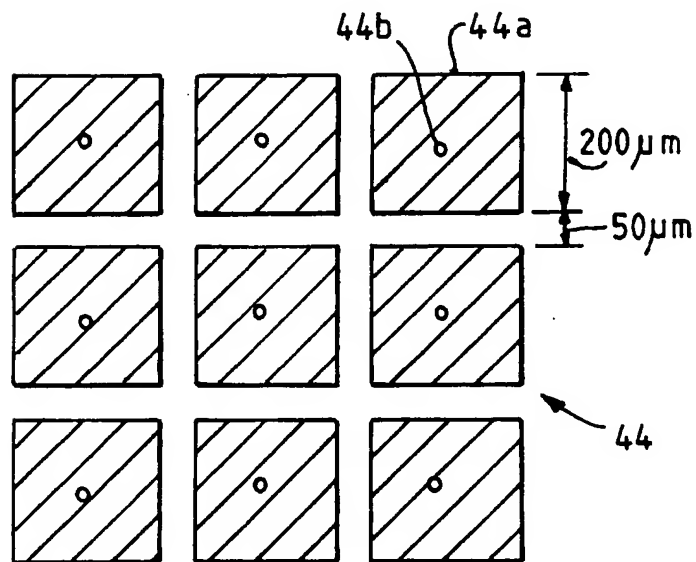


FIG. 16

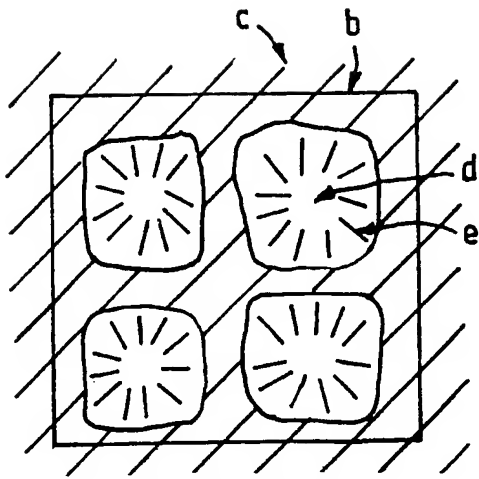


FIG. 17

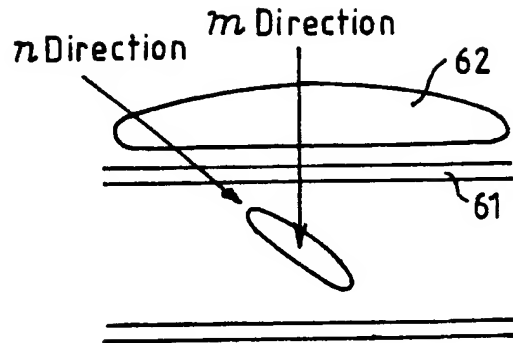


FIG. 18

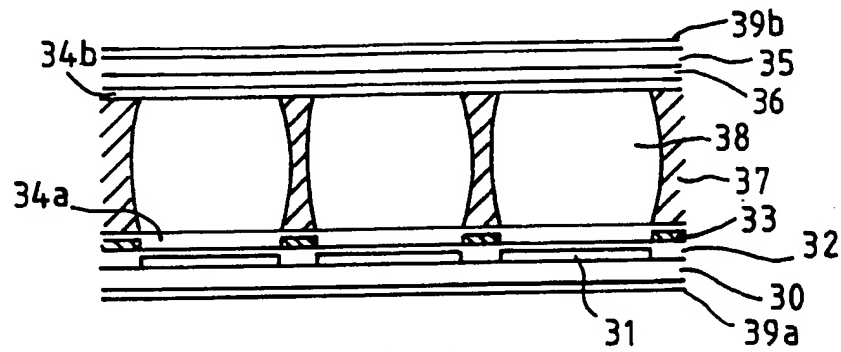


FIG. 19

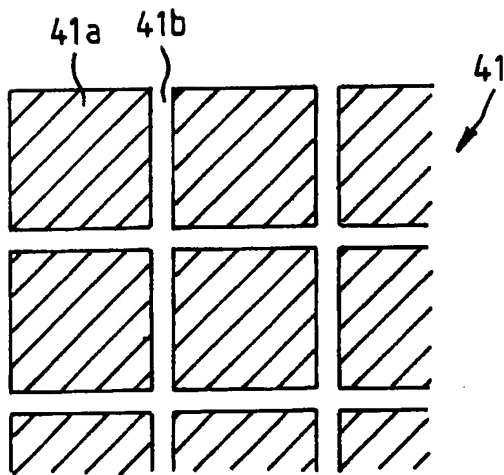
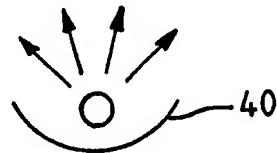


FIG. 20

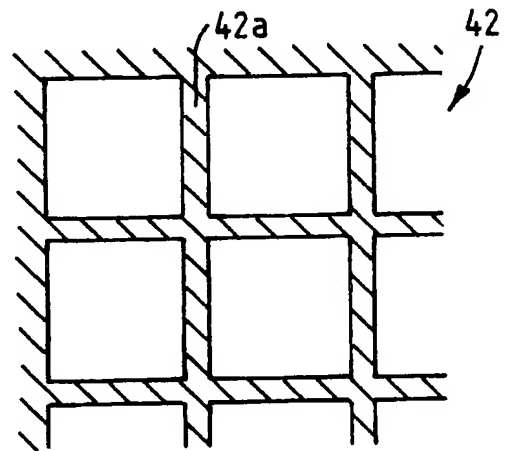


FIG. 21

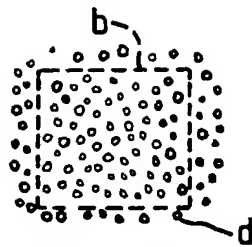


FIG. 22

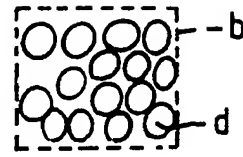


FIG. 23

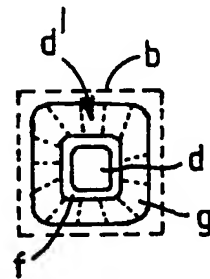


FIG. 24A

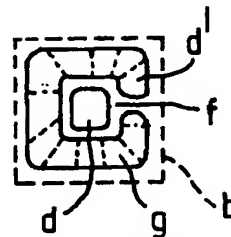


FIG. 24C

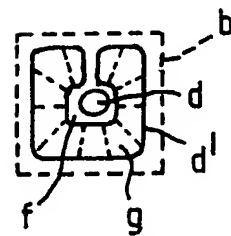


FIG. 24B

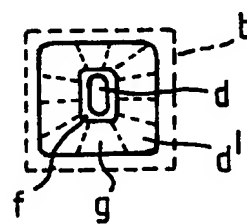


FIG. 24D

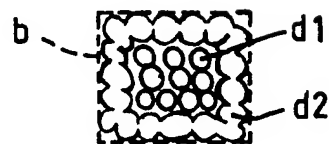
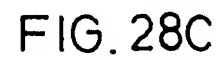
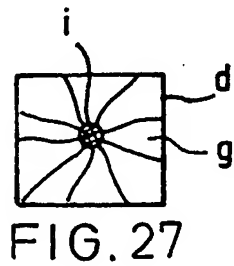
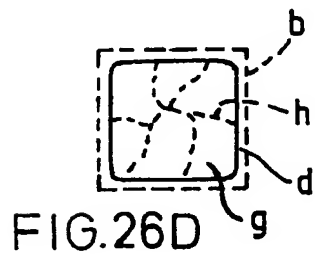
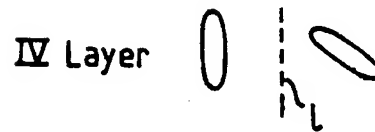
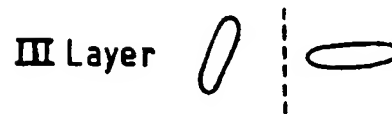
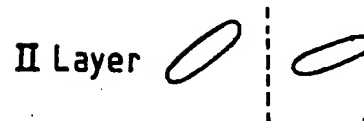
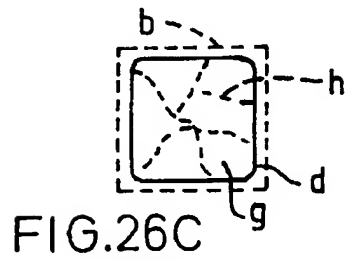
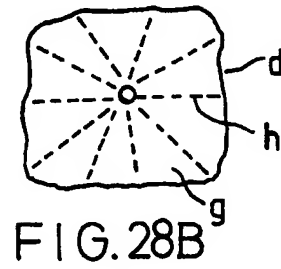
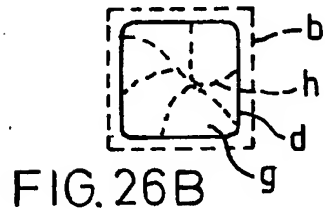
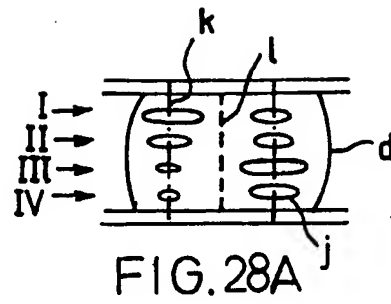
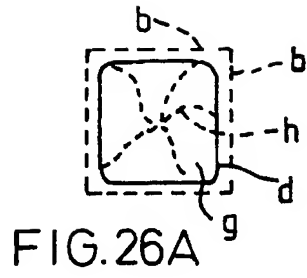


FIG. 25



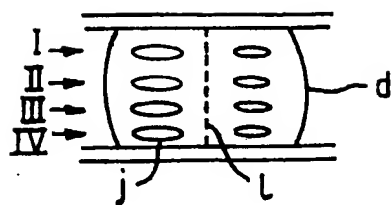


FIG. 29A

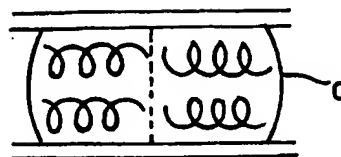


FIG. 30A

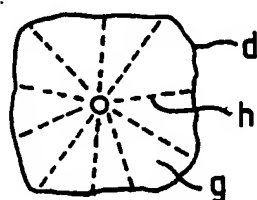


FIG. 29B

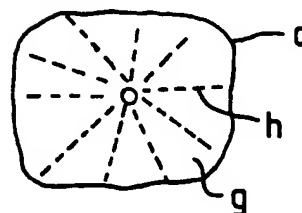


FIG. 30B

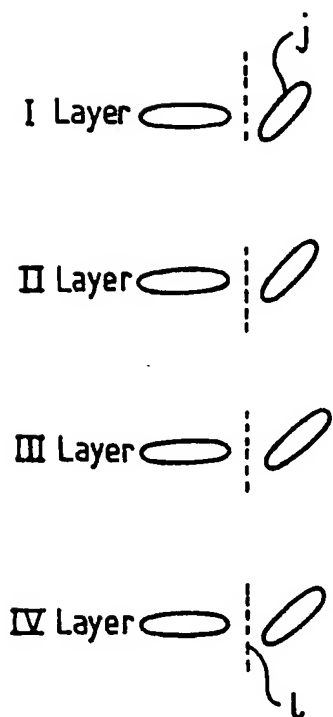


FIG. 29C

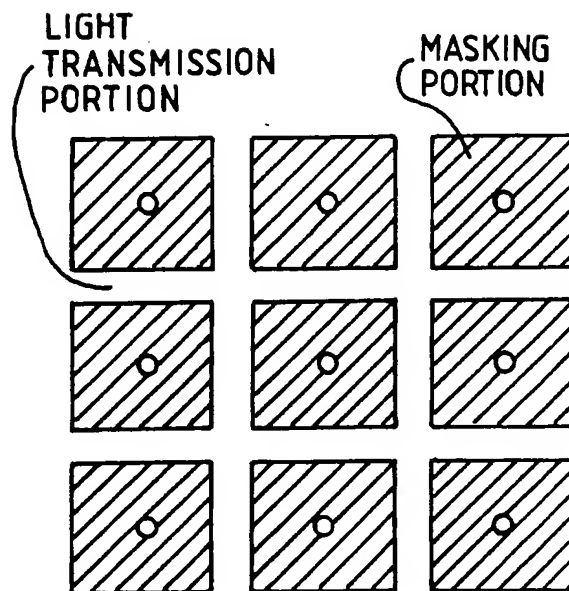


FIG. 31

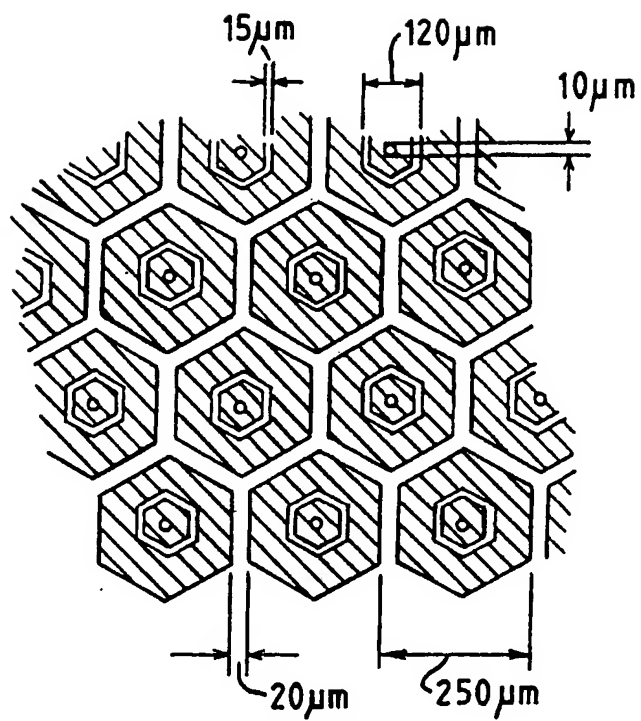


FIG. 32

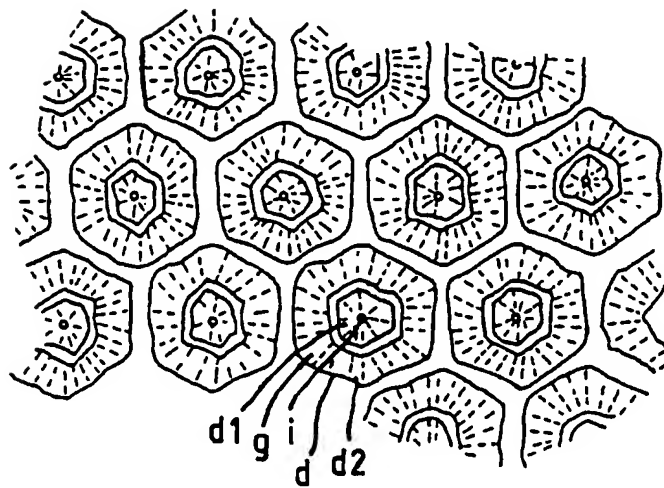


FIG. 33



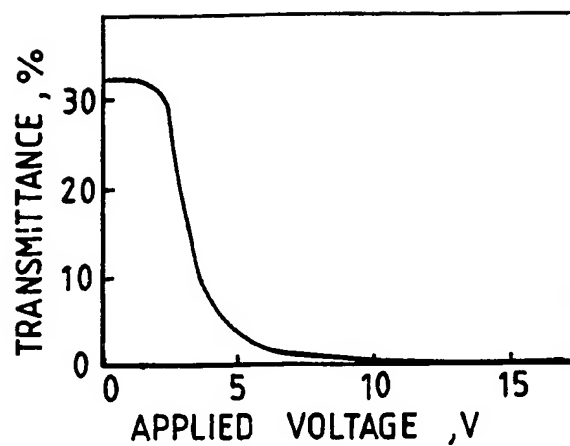


FIG. 34A

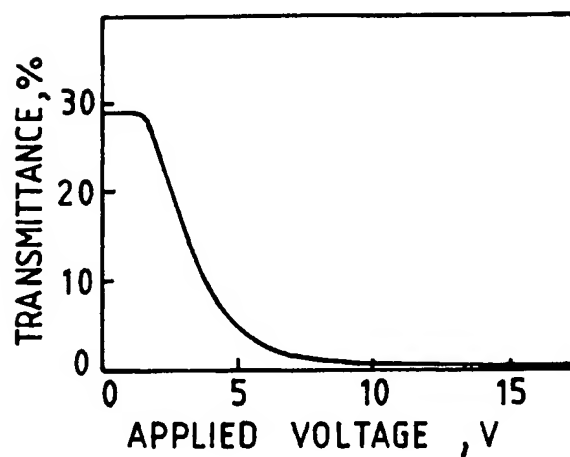


FIG. 34B

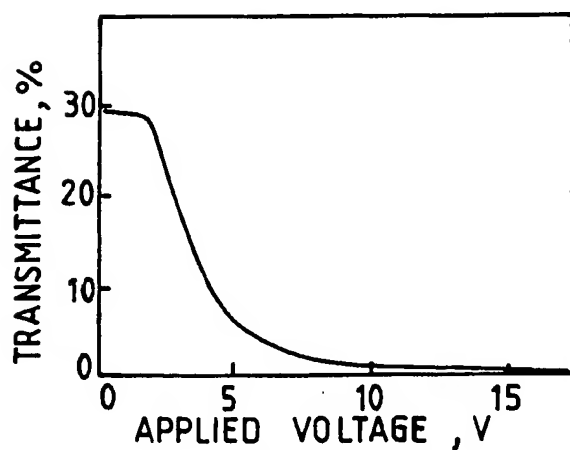
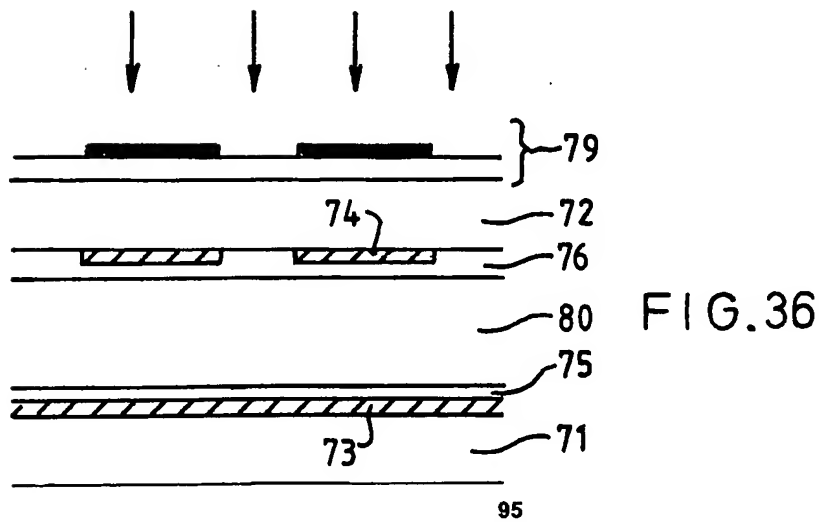
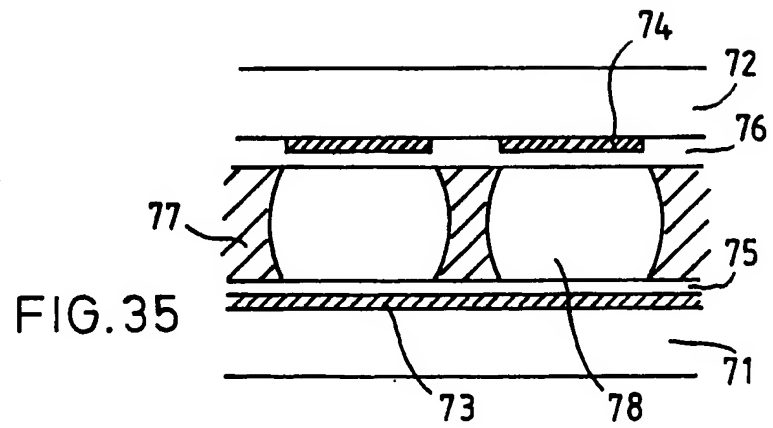
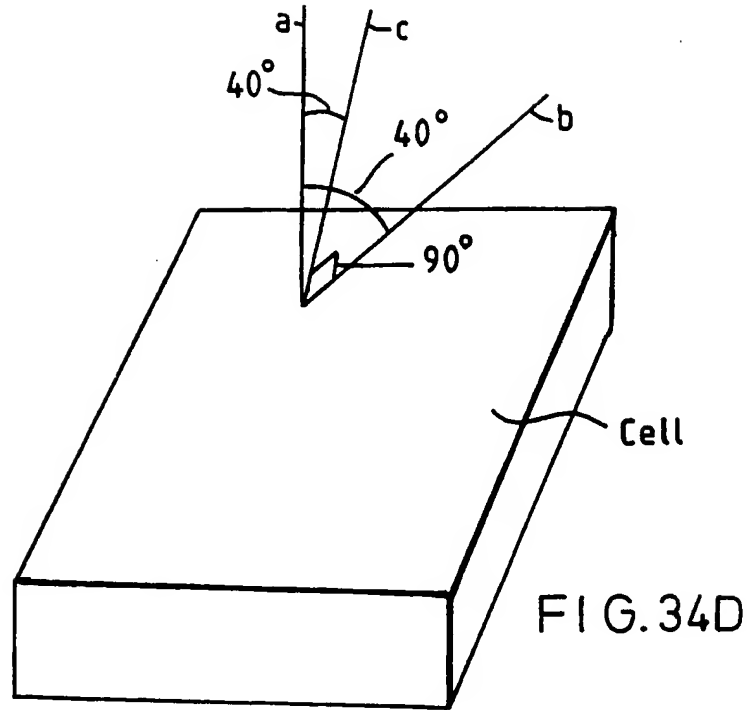


FIG. 34C



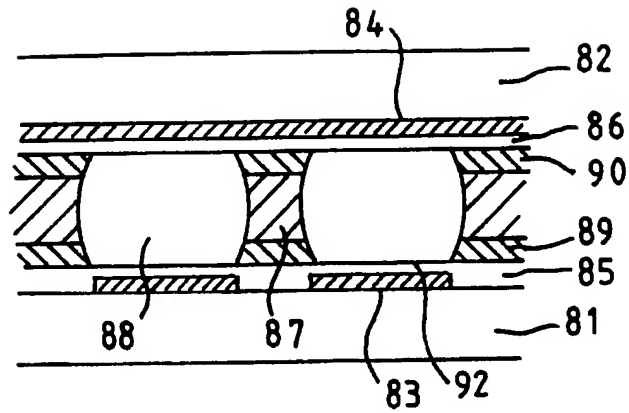


FIG. 37

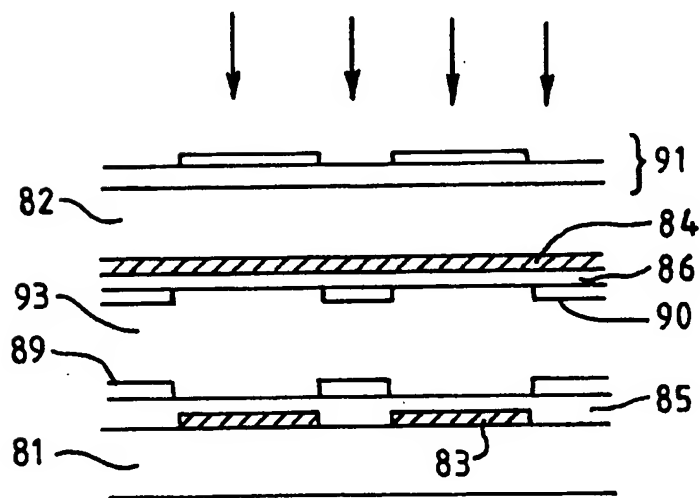


FIG. 38

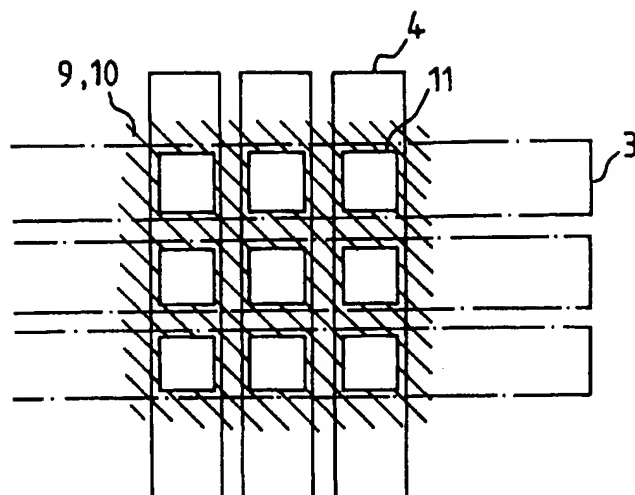


FIG. 39

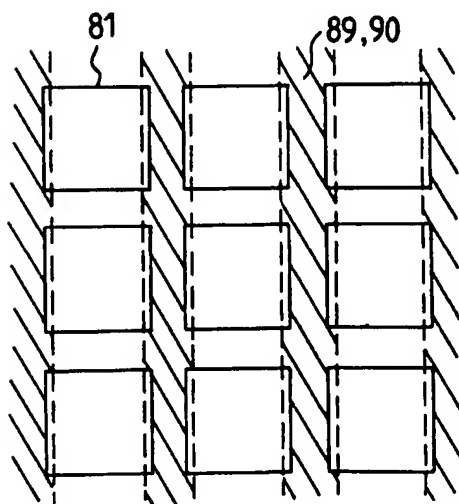


FIG. 40

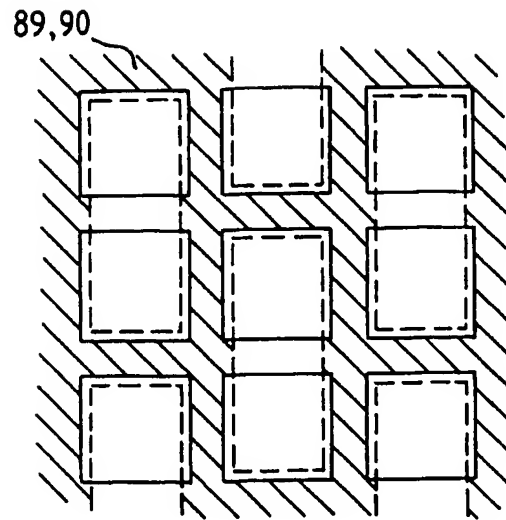


FIG. 41

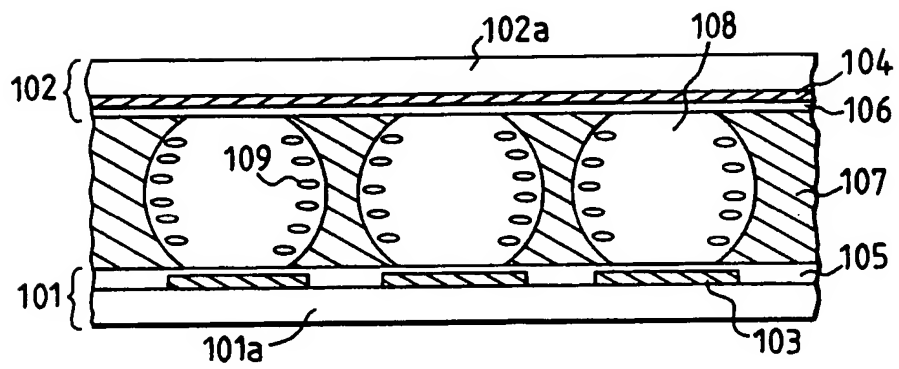


FIG. 42

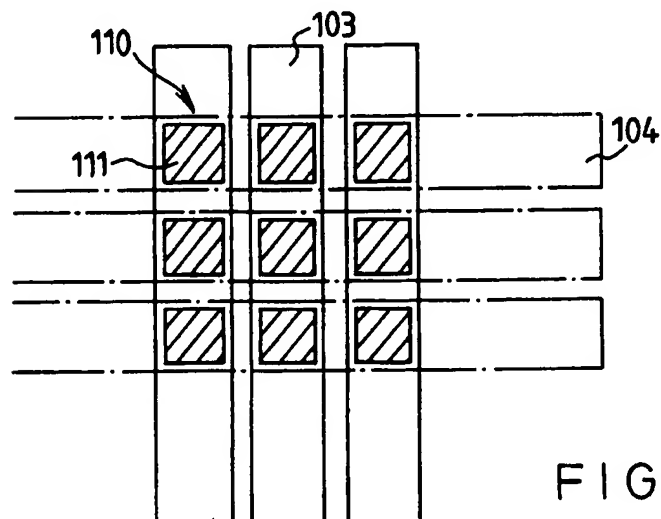


FIG. 43

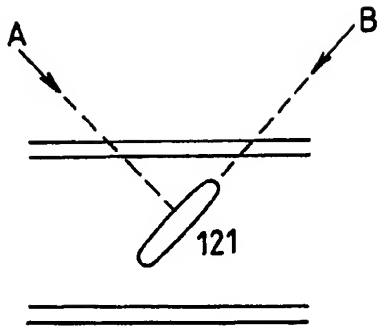


FIG. 44A

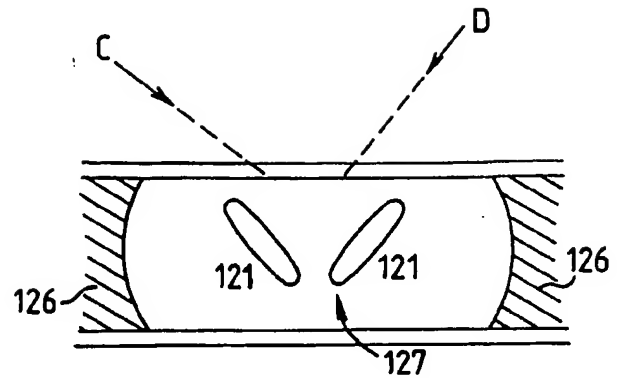


FIG. 44B

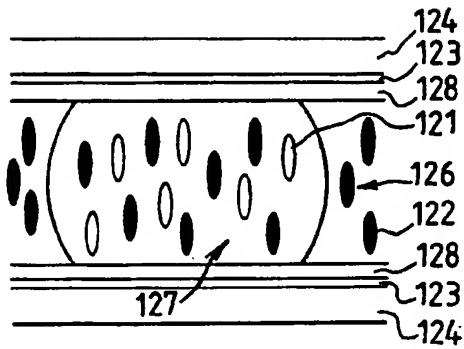


FIG. 45A

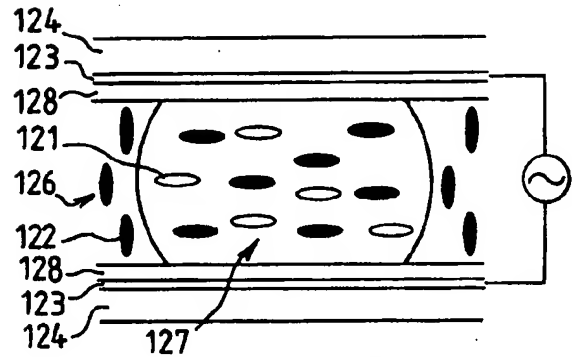


FIG. 45B

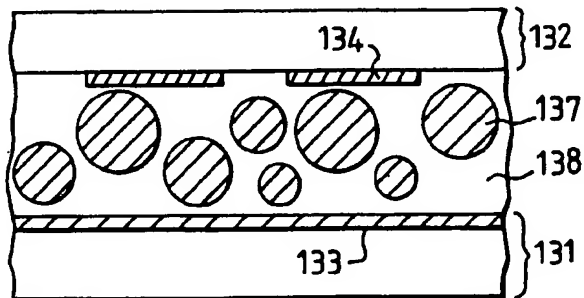
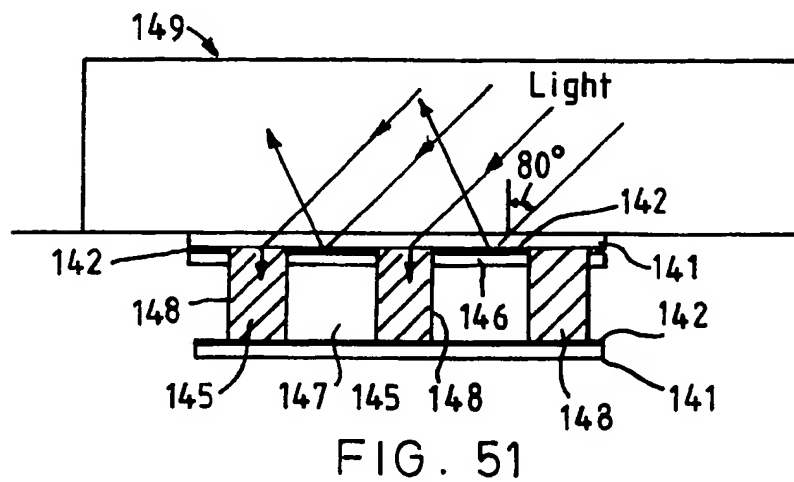
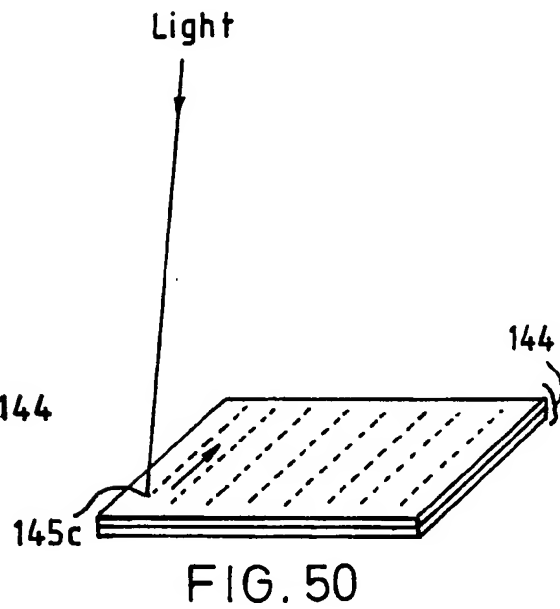
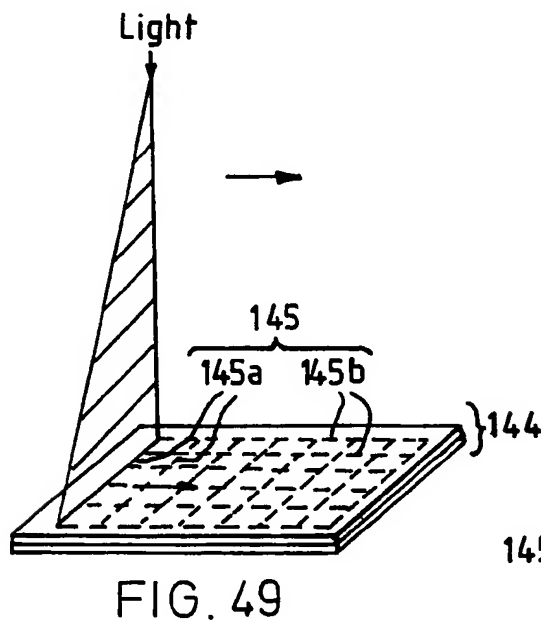
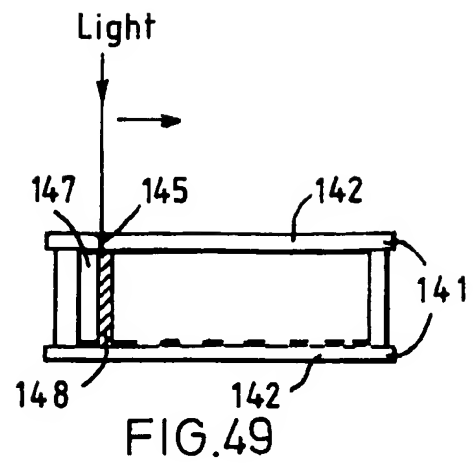
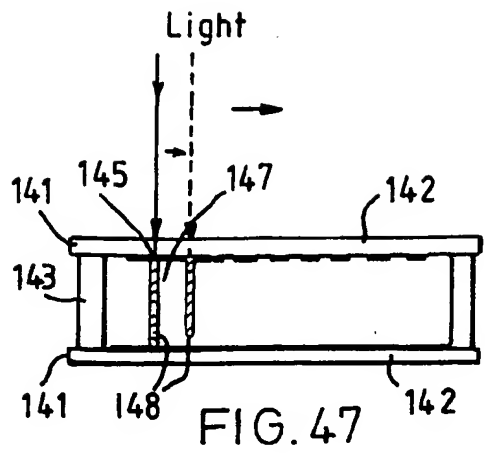


FIG. 46





Publication number : **0 568 355 A3**

**EUROPEAN PATENT APPLICATION**

Application number : 93303337.5

Date of filing : 28.04.93

Int. Cl.<sup>6</sup> : **G02F 1/1339, G02F 1/1333,  
G02F 1/1337, C09K 19/38,  
C09K 19/54**

- Priority : 28.04.92 JP 110223/92  
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 Kanmaki-cho  
 Kitakatsuragi-gun, Nara-ken (JP)  
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 Chuo-ku  
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 15-2, Shin-asahigaoka  
 Ikoma-shi, Nara-ken (JP)

Representative : **White, Martin David et al**  
**MARKS & CLERK,**  
 57/60 Lincoln's Inn Fields  
 London WC2A 3LS (GB)

**A liquid crystal display device and a method for manufacturing the same.**

A liquid crystal display device of the present invention includes : two substrates facing each other, at least one of the substrates being transparent ; electrodes disposed on inside surfaces of the respective substrates ; a display medium which is provided between the two substrates and formed of polymer walls (17) containing a polymer as their main component and liquid crystal regions (16) containing liquid crystal as their main component ; and a plurality of pixels, wherein the liquid crystal regions are partitioned by the polymer walls and are close to

the substrates, portions of the liquid crystal regions close to the substrates being in parallel with the substrates, an interval  $a$  between the center of one liquid crystal region and the center of an adjacent liquid crystal region in a direction along the surface of the substrate is within a width of one pixel along the direction, and 80% or more of the intervals  $a$  satisfy the relationship :  $3b/2 > a > b/2$ , where  $b$  is an average of the intervals  $a$ .

EP 0 568 355 A3





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 93 30 3337

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
X	US-A-4 295 712 (ISHIWATARI) * column 1, line 10 - column 2, line 37; figure 2 *	1,9,45, 46,48	G02F1/1339 G02F1/1333 G02F1/1337 C09K19/38 C09K19/54
X	GB-A-1 376 926 (SIEMENS) 11 December 1974 * page 2, line 35 - line 87; figures 4,6 *	1	
A,D	PATENT ABSTRACTS OF JAPAN vol. 14, no. 400 (P-1098) 29 August 1990 & JP-A-02 153 318 (TAKIRON CO) 13 June 1990 * abstract *	2,49	
E	EP-A-0 552 508 (N.V. PHILIPS) 28 July 1993 * column 2, line 17 - column 5, line 20 *	9,45,46, 48-52	
A	US-A-4 891 152 (MILLER) * column 5, line 39 - column 7, line 54 *	63,67,71	
A	JAPANESE JOURNAL OF APPLIED PHYSICS vol. 31, no. 38, 15 March 1992, TOKYO JP pages L352 - L354 E. SHIMADA 'CONTROL OF POLYMER ORIENTATION IN POLYMER DISPERSED LIQUID CRYSTAL' CHAPETRS : 21 AND 2.2	63,71	TECHNICAL FIELDS SEARCHED (Int. CL.5) G02F C09K
A	WO-A-89 09807 (DOANE) * page 09, line 33 - page 10, line 34 * * page 14, line 04 - line 23 *	80-82,84	
A	US-A-4 971 719 (VAZ ET AL) * column 1, line 45 - line 52 * * column 2, line 53 - line 59 *	89	
-/--			
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 March 1994	Examiner Diot, P
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	

EPO FORM 1503 (01.87) (P04C01)



European Patent  
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### CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid.
- namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

### LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,

namely:

see sheet -B-

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid.
- namely claims:
- ☐ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims.
- namely claims:



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 93 30 3337

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
P, A	DE-A-41 04 183 (MERCK) 30 July 1992 * page 4, line 10 - line 49 * * page 15, line 06 - page 17, line 45 * -----	89, 90, 92	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 March 1994	Examiner Diot, P
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (3.12.92) (P04C01)



European Patent  
Office

EP 93 30 3337 -B-

**LACK OF UNITY OF INVENTION**

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims 1-62:

A liquid crystal device having a plurality pixels comprising a display medium which is provided between two substrates and formed of polymer walls and liquid crystal region and a method of manufacturing by irradiating the mixture containing a liquid crystal and a photopolymerizable compound with a particular light distribution

2. Claims 63-79:

A method of manufacturing a liquid crystal device having a plurality of pixel, forming a film containing a photopolymerisation initiator on at least one substrate, providing a mixture containing a liquid crystal material and a polymerisable compound

3. Claims 80-88:

A method of manufacturing a liquid crystal device having a plurality of pixels providing a mixture containing a liquid crystal material and a photopolymerizable liquid crystalline material

4. Claims 89-95:

A method of manufacturing a liquid crystal device having a plurality of pixels providing a mixture of liquid crystal material a photopolymerizable compound a photopolymerization initiator and a radical generating agent

## Control of Polymer Orientation in Polymer Dispersed Liquid Crystal (PDLC)

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(Received December 7, 1991; accepted for publication January 18, 1992)

It is considered that electrooptical properties of polymer dispersed liquid crystal (PDLC) strongly depend on the polymer network structure. Therefore, we have tried to control the orientation of the polymer network of PDLC, and we succeeded by means of photopolymerization of the nematic phase mixture of the monomer and liquid crystal material. In addition, the liquid crystal in the PDLC was roughly aligned parallel to the extended direction of the polymer network. This result predicts that uniform alignment of liquid crystal can be obtained by optimizing the polymerization condition.

**KEYWORDS:** polymer dispersed liquid crystal, polymer orientation, UV-curable polymer, liquid crystal, display device, light scattering

### §1. Introduction

Polymer dispersed liquid crystals (PDLCs) have been studied by many workers recently. PDLCs are classified into two types: the microdroplet type,<sup>1,2)</sup> in which liquid crystal microdroplets are dispersed in a polymer matrix, and the polymer network type,<sup>3)</sup> in which liquid crystal is continuous in a polymer network. We have studied the polymer network type of PDLC.

One of the problems of conventional twisted nematic LCD is low brightness because of polarizers. In contrast, the PDLC does not need polarizers, and therefore, is capable of bright display. Other advantages of the PDLC are wide viewing angle, fast response and the absence of required surface treatment. On the other hand, it has some disadvantages, such as hysteresis in the voltage-transmittance curve, poor threshold sharpness and insufficient contrast due to relatively low scattering.

As for the problems of hysteresis and threshold sharpness, they are expected to be solved by controlling the orientation of the polymer network, because the alignment of liquid crystal in the PDLC is strongly affected by the polymer network structure. Therefore, for the first step of PDLC research, we have studied the orientation of the polymer network as well as the liquid crystal.

### §2. Experiment and Discussion

In the experiment, we used UV-curable diacrylate monomer doped with 2% of photoinitiator Darocure 1173 produced by Merck & Co. Inc. as a starting material of the polymer, and nematic liquid crystal PN-001 made by Daiippon Ink & Chemicals, Inc. These materials are reported by Fujisawa *et al.*<sup>3)</sup> to give low-voltage PDLC. A phase diagram of the mixture of monomer and liquid crystal is shown in Fig. 1. It is seen from this figure that the mixture becomes nematic in the region of high liquid crystal concentration. In this region, the monomer is considered to be oriented as in the case of the guest-host effect.<sup>4)</sup> Therefore we expected to be able to obtain an ordered polymer network structure by polymerization in

this region.

#### 2.1 Control of polymer orientation by rubbing treatment

As a typical sample, a mixture of 5% monomer and 95% liquid crystal which was nematic at 30°C was used in the experiment. This mixture was introduced into a cell composed of two glass plates with a gap of 9  $\mu\text{m}$  between them. The substrates were rubbed in advance with cloth in the direction parallel to each other. Then this cell was irradiated with UV light at 30°C to form the polymer network. After the polymerization, the cell was observed between crossed polarizers, and liquid crystal was found to be aligned roughly parallel to the rubbing direction.

In order to directly observe the polymer network structure, we removed the liquid crystal from the cell by extraction with methanol. Figure 2 shows a microphotograph of this sample. It is seen from this photograph that the polymer network extends in the rubbing direction.

Then, we measured the scattering property of the cell as a function of the polarization direction of incident light. The result is shown in Fig. 3 where the ordinate is the transmittance instead of the scattering for simplicity,

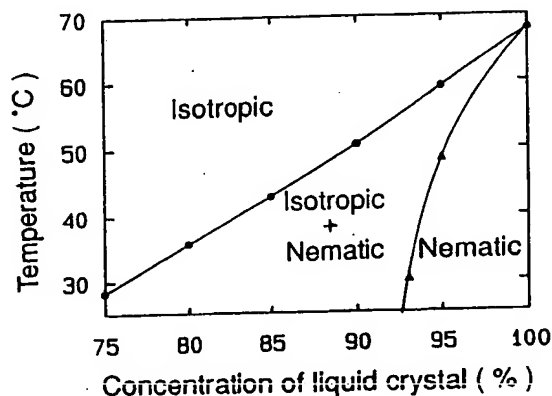


Fig. 1. Phase diagram of the mixture of liquid crystal and UV-curable monomer.

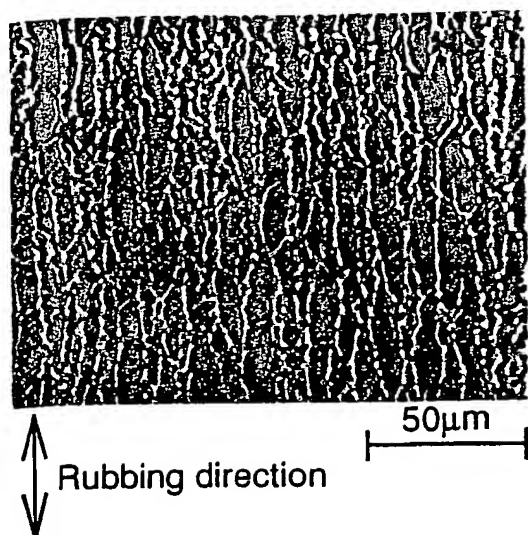


Fig. 2. Micrograph of the polymer network structure after removal of liquid crystal. The polymer network extends in the rubbing direction.

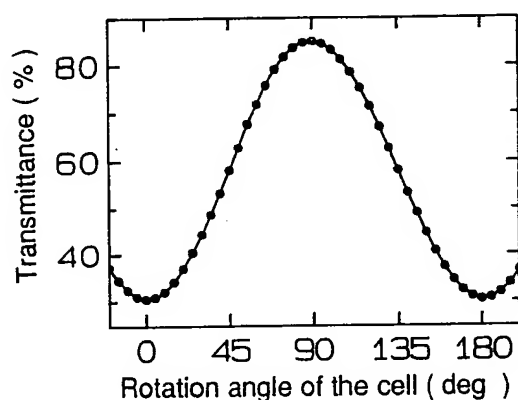
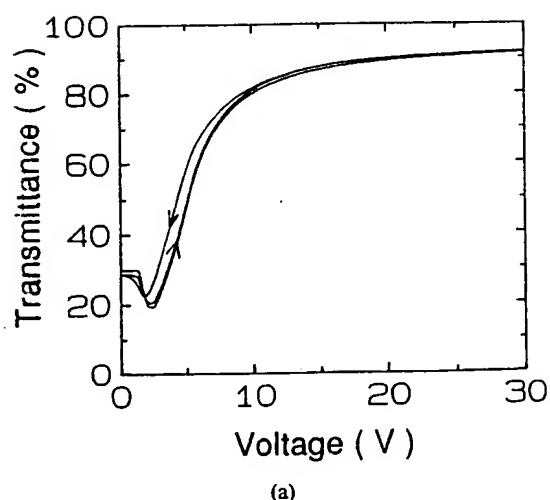
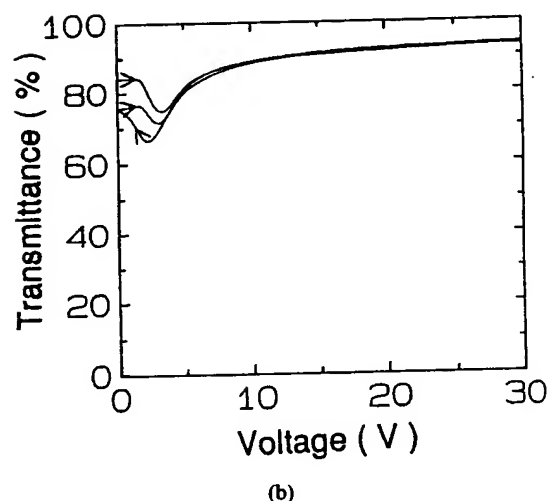


Fig. 3. Dependence of the transmittance on the polarization direction of the incident light (wavelength: 550 nm). Rotation angle indicates the angle between the polarization direction and the rubbing direction.

and the abscissa is the angle between the rubbing direction and polarization direction. It is seen that scattering becomes strongest and weakest when the polarization direction of incident light is parallel and perpendicular to the rubbing direction, respectively. This property is explained as follows. Liquid crystal is aligned parallel to the direction of the polymer network, and therefore, index mismatch between the liquid crystal and polymer becomes highest and lowest when the polarization direction is parallel and perpendicular to the rubbing direction, respectively. Figures 4(a) and 4(b) show the transmittance-voltage properties for the incident light polarized parallel and perpendicular to the rubbing direction, respectively. The high transmittance at high voltage in both condition is due to that liquid crystal is aligned perpendicular to the substrate and hence, the index mismatch becomes lowest. Incidentally, the transmittance shows a relatively small dip at 2~3 volts in both figures. It was found by microscopic observation that many domains arose in this voltage region. Therefore, the small dip in the transmittance is not due to the index



(a)



(b)

Fig. 4. Voltage-transmittance properties for the incident light polarized parallel (a) and perpendicular (b) to the rubbing direction (wavelength: 550 nm).

mismatch between the liquid crystal and polymer, but instead to the formation of domains.

## 2.2 Control of polymer orientation by electric field

In order to study the alignment effect of the electric field on the direction of the polymer network during polymerization, 50 volts was applied to the cell under the same conditions as mentioned in §2.1 and UV light was irradiated. The liquid crystal alignment of this PDLC was observed between crossed polarizers, and it was found that the alignment was almost perpendicular to the substrate but tilted slightly in the rubbing direction. In order to measure this angle, we measured the transmittance of the cell between the parallel polarizers by rotating the cell as shown in Fig. 5. The result is shown in Fig. 6. It is seen from this figure that the transmittance curves for different wavelengths commonly show symmetry with respect to  $\theta_0$ . This fact indicates that retardation becomes minimal at  $\theta_0$ , which gives the average direction of alignment. By using  $\theta_0$  and Snell's law, it was found that the alignment of liquid crystal was tilted from the perpendicular direction by about  $15^\circ$  toward the rubbing direction. This alignment did not change after

heating the cell over the clearing temperature of liquid crystal. Therefore, it is considered that the polymer network itself extends in this direction and that the liquid crystal is aligned along it.

In order to confirm the above speculation that the polymer network extends in the applied field direction, we fabricated another type of cell, to which an electric

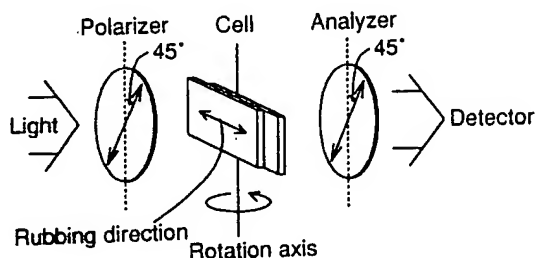


Fig. 5. Schematic illustration of the system to measure effective tilt angle of liquid crystal.

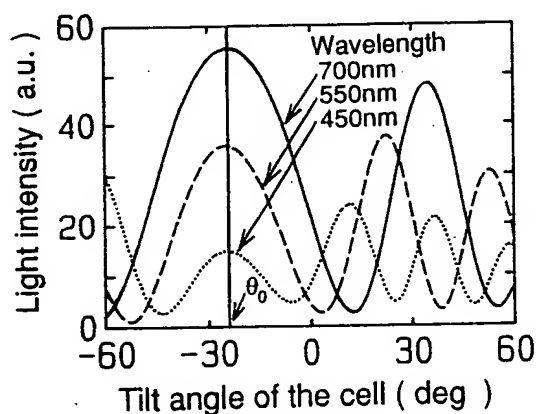


Fig. 6. Dependence of the transmitted light intensity of the cell between the parallel polarizers on the tilt angle.

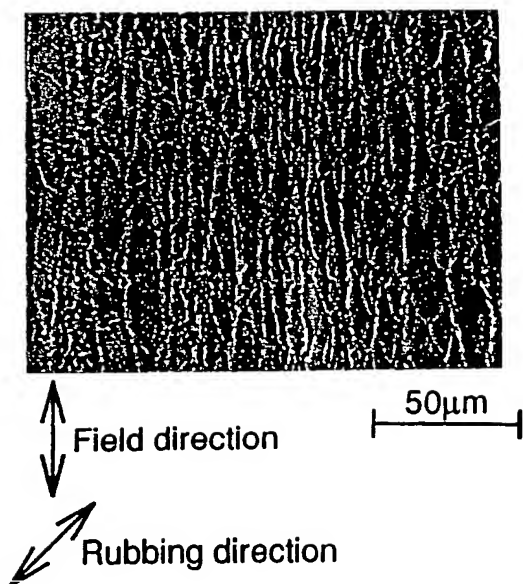


Fig. 7. Micrograph of the polymer network after removal of liquid crystal. The polymer network extends in the direction of the applied electric field.

field ( $1 \text{ V}/\mu\text{m}$ ) can be applied in the direction parallel to the surface but at an angle of  $45^\circ$  from the rubbing direction. Under the same conditions as mentioned in §2.1, except for the application of the electric field, UV light was irradiated to the cell. Then, we removed the liquid crystal by extraction with methanol and observed the polymer network through a microscope. Figure 7 is a microphotograph of the sample. We found that the polymer network did indeed extend in the applied field direction.

### §3. Conclusions

We succeeded in controlling the orientation of the polymer network by polymerization from a nematic phase mixture of monomer and liquid crystal material. There are two methods available to control the orientation direction. One method is the rubbing treatment of substrates, by which the nematic phase mixture is aligned parallel to the rubbing direction. Irradiation with UV light under this condition induced an extended polymer network into alignment parallel to the rubbing direction. The other method is the application of electric field during UV irradiation, which induced the polymer network into alignment parallel to the field. In contrast, it was confirmed that the polymer network structure was not aligned in a specific direction in the case in which polymerization was performed from the isotropic phase instead of the nematic phase. In addition, the liquid crystal in the PDLC, which was formed by the above-mentioned method, was aligned roughly parallel to the extended direction of the polymer network. It is predicted from this result that uniform alignment in an arbitrary direction can be obtained by optimizing the polymerization condition.

Incidentally, Araya *et al.*<sup>5-7)</sup> have also reported that they could orient polymer fibrils using liquid crystal by a different polymerization method. That is, a catalyst of polymerization was doped in the liquid crystal and the material of the polymer, acetylene gas, was introduced to the liquid crystal in a reactor. From this, we conclude that our method is more suitable for fabrication of PDLCs.

### Acknowledgements

We would like to express hearty thanks to Dainippon Ink & Chemicals, Inc. for the UV-curable monomer and liquid crystal, and to Dr. T. Miyashita for valuable discussion.

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# Induction of Liquid Crystal Orientation through Azobenzene-Containing Polymer Networks

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**ABSTRACT:** A diacrylate monomer containing a core of azobenzene groups was synthesized. Thermal polymerizations of mixtures of the monomer dissolved in a nematic liquid crystal, E7, resulted in liquid crystals stabilized by an azobenzene-containing polymer network. When their thin films were irradiated by linearly polarized UV light at room temperature, as a result of the alignment of azobenzene groups on the network, a macroscopic orientation of E7 molecules was induced perpendicular to the UV polarization direction. Infrared dichroism was used to measure the liquid crystal orientation in irradiated films. It was found that the achievable orientation, observed after minutes of irradiation, increases with increasing polymer network density and that a significant degree of the induced orientation remains stable after turning off the irradiation. This approach represents a new means to control the average liquid crystal orientation in materials such as polymer-stabilized liquid crystals.

## Introduction

Among liquid crystal-based electrooptical materials, polymer-stabilized liquid crystals (PSLC) show great potential for a number of applications including display technologies.<sup>1</sup> Generally, PSLC is prepared by first dissolving a small amount of monomers in a low molecular weight liquid crystal and then performing thermally or photoinduced polymerization giving rise to a polymer network. If the polymerization proceeded while liquid crystal molecules are oriented by surface treatment or effects of other external fields, the formed polymer network can be anisotropic. The network in turn can stabilize the liquid crystal orientation or a specific texture. This is the basis for electrically controllable light scattering of these materials, which is necessary for display applications. Chien and co-workers<sup>2,3</sup> have made PSLC with an azo-containing network and used the dichroic azo dyes to measure the optical order parameter of the aligned network. Unlike polymer-dispersed liquid crystals (PDLC), which consist of liquid crystal droplets in a polymer matrix, PSLC needs no match of refractive indices because of the low polymer concentration. Many studies have already been devoted to PSLC containing cholesteric and ferroelectric liquid crystals.<sup>1,4,5</sup>

The purpose of this study is to investigate possibilities of using irradiation to control or promote liquid crystal orientation in this type of materials. The basic idea is to make a polymer network carrying azobenzene groups which not only can stabilize liquid crystal but also alter its orientation through irradiation. In recent years, azobenzene-containing polymers and liquid crystalline polymers have attracted a lot of attention.<sup>6-10</sup> They have the potential to be used as optical storage media. The basis of all the interests is the photoinduced isomerization of azobenzene. Among the many studies exploring the use of this phenomenon,<sup>6-12</sup> it has been shown that this photoisomerization can induce isothermal nematic to isotropic phase transition in liquid crystalline poly-

mers<sup>10</sup> and can induce orientation of azobenzene moieties.<sup>7</sup> When linearly polarized light irradiates a thin film of azobenzene polymers, the azobenzene groups tend to be aligned perpendicular to the polarization direction. The orientation mechanism is now understood. Upon irradiation, each photoinduced trans-cis isomerization is followed by thermally activated cis-trans isomerization, which causes a small reorientation of the transition moment. After a large number of the trans-cis-trans cycles, the result is a preferential orientation of azobenzene groups normal to the polarization plane. The ability for azobenzene groups to induce orientation of nonreactive units has been well demonstrated.<sup>13</sup>

From the above, if a liquid crystal is stabilized by a polymer network carrying azobenzene groups, it is conceivable that any azobenzene orientation due to irradiation could alter the director fields of surrounding liquid crystal molecules, leading to their orientation. If this is true, the approach is of interest, considering the importance of controlling the average liquid crystal orientation over macroscopic length scales. The method can add an additional means to promote and manipulate liquid crystal orientation in PSLC. In contrast with surface alignment, a polymer network offers "volume" or "bulk" effects, which could have the advantage, for instance, to align liquid crystals in relatively thick films. Furthermore, aligning liquid crystals through irradiation of the polymer network gives selectivity for the orientation that surface treatment cannot. As azobenzene groups are aligned only in areas exposed to irradiation, the orientation of liquid crystal molecules should occur only in those areas. Combined with surface alignment, an irradiation-controllable orientation could give PSLC materials more possibilities for design of electrooptical properties. In addition to PSLC, the approach can be of general interest in the search of electrooptical materials, for which the basis of applications is often the induction and control of birefringence.

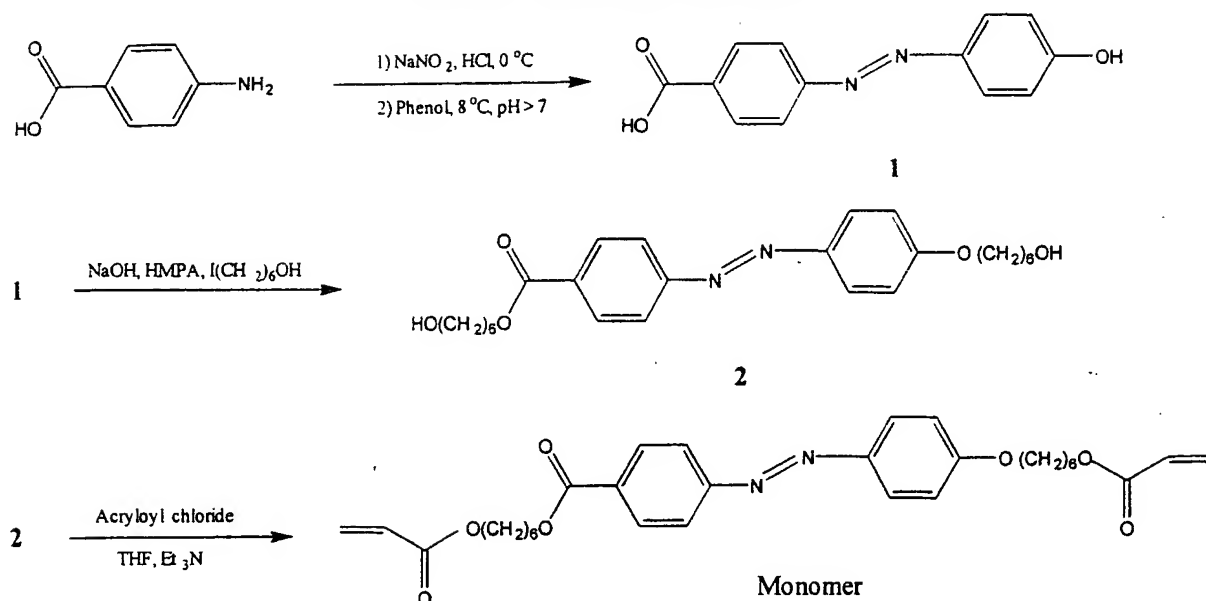
In this paper, we report our investigations on a system of liquid crystal/azobenzene-polymer network. A diacrylate monomer having an azobenzene moiety as the central core was synthesized for the purpose. It will

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Scheme 1. Synthesis of Monomer



be shown that thermal polymerizations of mixtures of liquid crystal/monomer led to the formation of a homogeneous polymer network stabilizing the liquid crystal. Irradiation by a linearly polarized UV light could indeed induce orientation of liquid crystal molecules surrounding the network. The orientation was characterized using infrared dichroism.

### Experimental Section

**Synthesis of the Diacrylate Monomer.** The synthetic route used to prepare the diacrylate monomer carrying an azobenzene group is shown in Scheme 1. It is interesting to notice that the monomer does not have a symmetrical chemical structure, possessing an ether group on one side and an ester group on the other side of the azobenzene core. The six methylene spacers on both sides are quite long, which should give the azobenzene group enough freedom for conformational changes and movement. Starting chemicals for the synthesis, such as 4-aminobenzoic acid, phenol, 6-chlorohexanol, and acryloyl chloride, were purchased from Aldrich and used as received. All compounds were characterized by differential scanning calorimeter (DSC) and a number of spectroscopic techniques including infrared (IR), ultraviolet (UV), proton nuclear magnetic resonance ( $^1\text{H}$  NMR), and mass spectroscopy. Details on the synthesis and characterization results are summarized below.

**4-(p-Hydroxyphenylazo)benzoic Acid (1).** Obtained through diazonium coupling between the diazonium salt of 4-aminobenzoic acid and phenol. After several recrystallizations from ethanol, **1** was obtained with good yield of about 66%. Mp: 276 °C. MS ( $m/e$ ): 242 ( $M^+$ ). UV  $\lambda/\text{nm}$  (methanol): 376 ( $\pi \rightarrow \pi^*$ , diazobenzene), 1708 ( $\text{C}=\text{O}$ ), 1599 (phenyl), 1418, 1237, and 1289 ( $\text{C}-\text{O}$ , benzoic acid).  $^1\text{H}$  NMR  $\delta/\text{ppm}$  (acetone- $d_6$ ,  $J/\text{Hz}$ ): 11.3 (br, 1H), 9.25 (br, 1H), 8.20 (d,  $J$  8.5, 2H), 7.94 (d,  $J$  8.5, 2H), 7.91 (d,  $J$  8.9, 2H), 7.04 (d,  $J$  8.9, 2H).

**6-Hydroxyhexyl 4-[p-(6-Hydroxyhexyloxy)phenylazo]benzoate (2).** Alkylation, with 6-iodohexanol, of both carboxylic acid and phenol functions of **1** occurred simultaneously in HMPA, using a NaOH solution as the deprotonating agent. Under these conditions, decarboxylation caused by NaOH was minimized. 6-Iodoheanol was preferred to the analogous chloro compound for improved yield and reduced reaction time. (6-Iodoheanol was prepared by reaction of 6-chlorohexanol with sodium iodide in acetone under reflux.) The typical procedure was as follows. To a solution of 1.0 g of **1** (4.1 mmol) in 13 mL of HMPA was added 1.1 mL of aqueous 33% NaOH solution (9.1

mmol). The solution was stirred for 0.5 h at 5 °C; then, 2.66 g of 6-iodohexanol (11.7 mmol) was added, and the solution was stirred for 4 days at room temperature (20–25 °C). The mixture was poured into 200 mL of water, and the precipitate formed was filtered, dried, and dissolved in chloroform. This solution was washed three times with water and then dried over anhydrous sodium sulfate overnight. Solvent was removed under reduced pressure. The product of **2** was purified by several recrystallizations from toluene, and the yield was 38%. Mp: 107 °C; clearing point: 123 °C (a smectic mesophase between 107 and 123 °C). MS ( $m/e$ ): 442 ( $M^+$ ). UV  $\lambda/\text{nm}$  (methanol): 360 ( $\pi \rightarrow \pi^*$ , diazobenzene), 442 ( $n \rightarrow \pi^*$ ). IR  $\nu/\text{cm}^{-1}$  (KBr): 3600–3100 ( $-\text{OH}$ ), 1708 ( $\text{C}=\text{O}$ ), 1599 (phenyl), 1277 and 1251 ( $\text{C}-\text{O}$  benzoate).  $^1\text{H}$  NMR  $\delta/\text{ppm}$  ( $\text{CDCl}_3$ ,  $J/\text{Hz}$ ): 8.17 (d,  $J$  8.5, 2H), 7.94 (d,  $J$  9.0, 2H), 7.90 (d,  $J$  8.5, 2H), 7.01 (d,  $J$  9.0, 2H), 4.35 (t,  $J$  6.6, 2H), 4.06 (t,  $J$  6.5, 2H), 3.68 (t,  $J$  6.5, 2H), 3.67 (t,  $J$  6.5, 2H), 1.79–1.85 (m, 4H), 1.53–1.65 (m, 4H), 1.35–1.49 (m, 8H).

**6-Acryloyloxyhexyl 4-[p-(6-Acryloyloxyhexyloxy)phenylazo]benzoate (3).** Monomer **3** was obtained by esterification of **2** with acryloyl chloride. A stoichiometric amount of acryloyl chloride was added for reaction of the two alcohol functions carried by **2**. For a typical reaction, 0.27 g of acryloyl chloride (2.9 mmol) in 0.7 mL of anhydrous THF was added dropwise under nitrogen and at 0 °C, to a stirred solution containing 0.5 g of **2** (1.1 mmol) and 0.24 g of triethylamine (2.9 mmol) in 7 mL of anhydrous THF. The stirring was continued for 6 h at 0 °C; then the solvent was removed and the residue dissolved in  $\text{CH}_2\text{Cl}_2$ . This solution was washed with water and aqueous 10%  $\text{NaHCO}_3$  solution and dried over anhydrous sodium sulfate overnight. The crude product was dissolved in hexane, and the solution was washed with water and dried over anhydrous sodium sulfate before solvent was removed under reduced pressure. A yield of about 70% was obtained. Mp: 51 °C. MS ( $m/e$ ): 550 ( $M^+$ ). UV  $\lambda/\text{nm}$  (methanol): 358 ( $\pi \rightarrow \pi^*$ , diazobenzene), 442 ( $n \rightarrow \pi^*$ ). IR  $\nu/\text{cm}^{-1}$  (KBr): 1721 ( $\text{C}=\text{O}$ , acrylate), 1703 ( $\text{C}=\text{O}$ , benzoate), 1632 ( $\text{C}=\text{C}$ ), 1601 and 1501 (phenyl), 1405 ( $\text{C}=\text{CH}_2$ ), 1286 and 1252 ( $\text{C}-\text{O}$  carboxylic esters), 1272 and 1199 ( $\text{C}=\text{C}$ ).  $^1\text{H}$  NMR  $\delta/\text{ppm}$  ( $\text{CDCl}_3$ ,  $J/\text{Hz}$ ): 8.16 (d,  $J$  8.5, 2H), 7.94 (d,  $J$  9.0, 2H), 7.90 (d,  $J$  8.5, 2H), 7.00 (d,  $J$  9.0, 2H), 6.40 (d,  $J$  17.3, 2H), 6.07–6.17 (m,  $J$  10.4, 17.3, 2H), 5.82 (d,  $J$  10.4, 2H), 4.35 (t,  $J$  6.6, 2H), 4.18 (t,  $J$  6.6, 2H), 4.06 (t,  $J$  6.4, 2H), 1.78–1.89 (m, 4H), 1.68–1.77 (m, 4H), 1.44–1.59 (m, 8H).

**Polymerization.** A nematic liquid crystal, E7, was purchased from EM Industries and used in this study. E7 is a eutectic liquid crystal mixture of four cyanobiphenyl compounds containing an alkyl group.<sup>14</sup> E7 has a clearing tem

Table 1. Characteristics of the Reacting Mixtures of Monomer and E7

mixture	E7 (wt %)	monomer (wt %)	AIBN (wt %)	azobenzene/cyanobiphenyl (mole ratio)
1	93.8	4.9	1.3	2.6
2	88.1	10.7	1.2	6.0
3	78.9	19.1	2.0	11.9

perature  $T_{ni} \sim 58^\circ\text{C}$ . To prepare E7 stabilized by azobenzene-containing polymer network, a mixture was first obtained by dissolving, in E7, the desired amounts of the monomer as well as the initiator, azobis(isobutyronitrile) (AIBN). The mixture was warmed to about  $45^\circ\text{C}$ , which allowed a complete dissolution of the monomer and AIBN in the liquid crystal without initiating the polymerization. Afterward, the polymerization proceeded by placing a drop of the E7/monomer mixture between two  $\text{CaF}_2$  windows (transparent to IR and UV) and heating the whole to  $80^\circ\text{C}$ . After 6 h of polymerization, the sample was cooled to room temperature. It was found that such a thermally induced polymerization of the monomer led to a homogeneous network stabilizing the liquid crystal. The resulting film lost the fluidity of the mixture before the reaction and became pasty. Listed in Table 1 are the compositions of the three mixtures used for polymerization. They resulted in E7/network samples of different densities of the azobenzene-containing network. Acronyms of E7/monomer-95/5, E7/monomer-90/10, and E7/monomer-80/20 are used in the paper because the actual concentrations of the monomer in the mixtures were close to 5, 10, and 20 wt %. For the same reason, similar acronyms are used for the E7/network samples. The approximate mole ratios of the groups of azobenzene (in the network) to cyanobiphenyl (liquid crystal molecules) are also indicated in Table 1. All the polymerizations resulted in thin films of a similar thickness of  $5\text{--}6\ \mu\text{m}$ , which was estimated by measuring the thickness of the two  $\text{CaF}_2$  windows with and without the film using a digital micrometer.

A number of attempts were made to perform photoinduced polymerization, but they all failed to produce a homogeneous network. The failure was caused by the particular monomer synthesized for this study. The monomer has a strong UV absorption centered at  $358\ \text{nm}$ , which is close to the absorption of the photoinitiator (benzoin methyl ether) near  $326\ \text{nm}$ . As a combined result of the very high extinction coefficients and the large amount of the monomer as compared to the case of the photoinitiator, the latter could not absorb light efficiently and was unable to initiate the polymerization. Using an excess amount of the photoinitiator and prolonged reaction times, polymer networks were eventually obtained, but they were phase separated from E7 and could not stabilize the liquid crystal. Irradiation of those phase-separated azobenzene networks in E7 resulted in no molecular orientation, contrary to the network prepared from thermal polymerization.

**Irradiation and Orientation Measurements.** Using a 50 W xenon lamp and a polarizer, films of E7/network were irradiated, at preselected areas, by linearly polarized light at room temperature. The used irradiation wavelength,  $\lambda = 358\ \text{nm}$ , was selected through the use of two monochromators. Intensity and width of irradiation were adjusted by using filters and two slits; the intensity was about  $2\ \text{mW}/\text{cm}^2$ . Typically, after a film was irradiated for a certain time, the radiation was turned off. The film was then installed in the IR spectrometer for the dichroism measurements. The same film could be irradiated again at the same area. (The rest of the film was masked.) Irradiated areas became visibly transparent, while nonirradiated areas appeared translucent.

As mentioned above, polarized irradiation should align azobenzene groups on the network. This orientation, unfortunately, could not be measured directly from IR dichroism because of the low concentrations of the network (no suitable bands). UV dichroism could also not be employed because of too strong UV absorption. Instead, IR dichroism could monitor any macroscopic orientation of E7 molecules that surround the network, which was the main interest of this

study. The absorption band of cyano end groups on liquid crystal molecules such as E7, near  $2230\ \text{cm}^{-1}$ , is often used to determine the order parameter  $S$  through<sup>15</sup>

$$S = (3\langle \cos^2 \Theta \rangle - 1)/2 = (R - 1)/(R + 2)$$

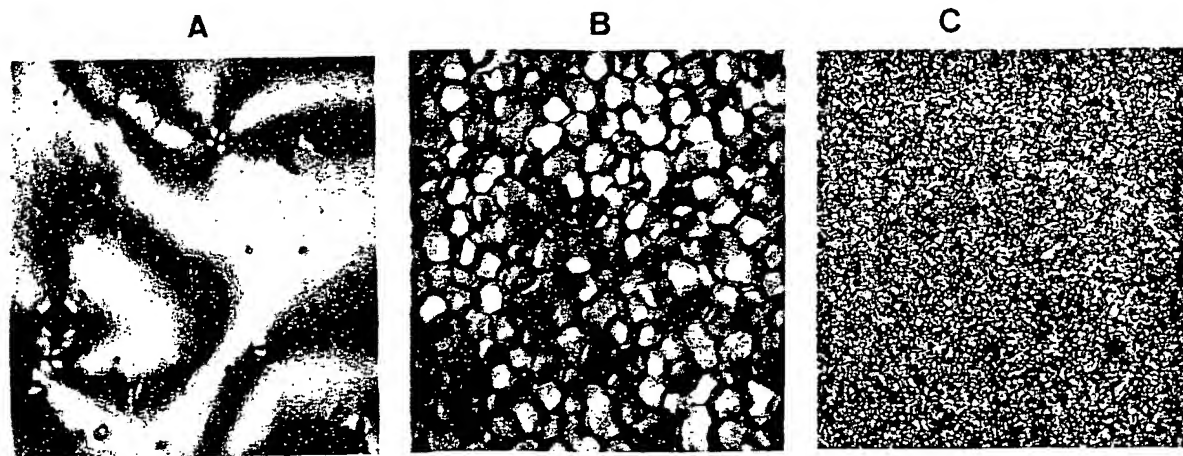
where  $\Theta$  is the angle between the long axes of liquid crystal molecules and a reference direction, e.g., the UV polarization direction;  $R = A_{\parallel}/A_{\perp}$ ,  $A_{\parallel}$  and  $A_{\perp}$  being the absorbances of the  $2230\ \text{cm}^{-1}$  band with the infrared beam polarized parallel and perpendicular, respectively, to the reference direction.  $S$  measures the average molecular orientation and can have values between  $-0.5$  and  $1$ .  $S = 1$  means a perfect orientation parallel to the reference direction, while a perfect perpendicular orientation gives  $S = -0.5$ .  $S = 0$  indicates the absence of any macroscopic orientation, which is the case for liquid crystals having a polydomain texture.

Polarized IR spectra were recorded on a Bomem MB-102 FTIR spectrometer, with a wire-grid polarizer placed between the sample and the DTGS detector. Phase transition temperatures were determined using a Perkin-Elmer DSC-7 apparatus with a heating rate of  $10^\circ\text{C}/\text{min}$ . Morphologies as well as changes in birefringence were examined on a Leitz DMR-P polarizing microscope, equipped with an Instec hot stage. Other apparatus used for characterizations were a Bruker AC-300 NMR spectrometer and a HP 8452A UV-vis spectrophotometer.

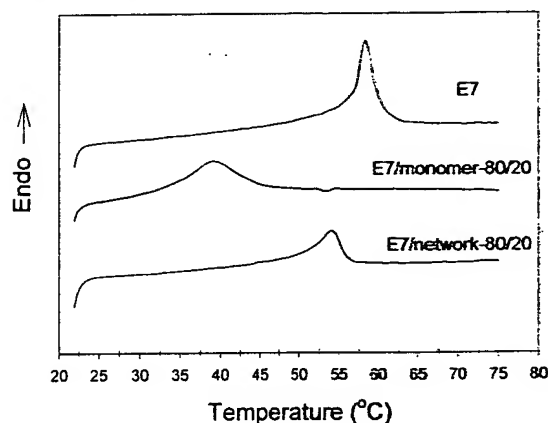
## Results and Discussion

Figure 1 shows a series of photomicrographs taken under crossed polarizers at room temperature. Before polymerization, the reactive mixture of E7/monomer-90/10 displayed a typical schlieren texture, with some large defects developed. After 50 min of polymerization, the morphology of the mixture changed drastically. Even though the polymerization was incomplete, more defects appeared, and a sort of network could be seen. After 5 h of reaction, the polymerization was essentially completed. The texture of E7/network looked very much like a nematic side-chain liquid crystalline polymer, and no phase-separated polymer was observed. These results suggest the formation of a homogeneous polymer network throughout the sample. As the network structure developed with time, the director fields of E7 were continuously altered. In the end, defects could develop with the presence of a disordered polymer network, which led to an apparently fine texture. Similar results were obtained for other samples. An example of DSC results is also given to show the effects of the network formation. Figure 2 compares the DSC heating curves for pure E7, E7/monomer-80/20, and E7/network-80/20. Before the polymerization,  $T_{ni}$  of E7 in the mixture was reduced by about  $20^\circ\text{C}$  below  $T_{ni}$  of pure E7, and the transition peak was much broadened. This indicates an extensive mixing and interaction between the two compounds. After the polymerization, without observable phase separation,  $T_{ni}$  of E7 raised to only  $4^\circ\text{C}$  below that of pure E7. Such an effect is characteristic of a polymer solubilized in liquid crystals.

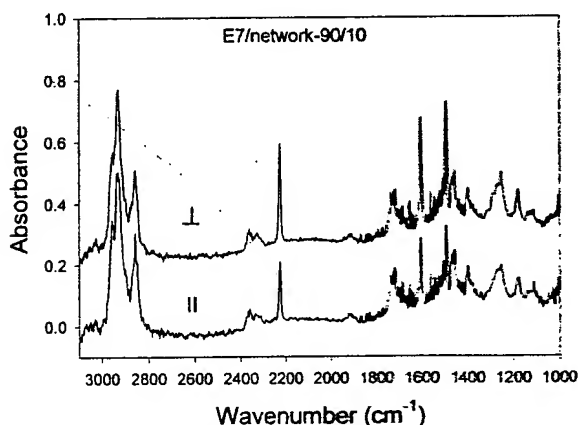
Indeed, a macroscopic orientation of E7 molecules can be induced in areas irradiated by a linearly polarized UV light. A qualitative analysis of polarized IR spectra can reveal interesting features of this orientation. Figure 3 shows the two IR spectra for a  $6\ \mu\text{m}$  film of E7/network-90/10, taken with IR beam polarized parallel and perpendicular to the UV polarization. The film was irradiated for 30 min. The strong perpendicular dichroism for the bands at  $2227\ (\text{CN})$ ,  $1606$ , and  $1494\ \text{cm}^{-1}$  (phenyl) indicates orientation of E7 molecules perpendicular to the UV polarization. It is therefore



**Figure 1.** Polarized optical micrographs ( $250\times$ ) for E7/monomer-90/10 mixture at room temperature: before polymerization (A), 50 min after polymerization (B), and 5 h after polymerization (C).

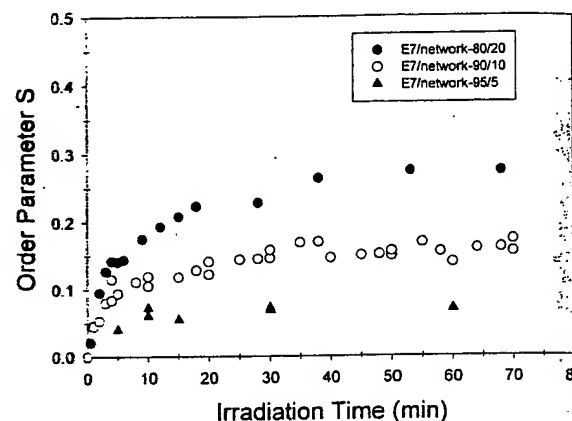


**Figure 2.** DSC heating curves for pure E7 and E7/monomer-80/20 mixture before and after polymerization.



**Figure 3.** Polarized infrared spectra for an E7/network-90/10 film irradiated for 30 min at room temperature. The two spectra were recorded with the electric vector of the infrared beam parallel (||) and perpendicular (⊥) to the polarization direction of UV irradiation.

clear that alignment of azobenzene groups on the network alters the director fields of liquid crystal molecules and orients them along the same direction. Interestingly, this is true not only for the rigid biphenyl cores of E7, as probed by the CN and phenyl bands, but also for their flexible alkyl groups. Although less important, a parallel dichroism<sup>16</sup> can be noticed for the  $\text{CH}_2$  bands at 2856 and 2929  $\text{cm}^{-1}$ , which arise mostly from the alkyl spacers of E7 molecules because of the dominant concentration of E7 in the mixture. On the



**Figure 4.** Order parameter of E7 vs irradiation time for samples having different azobenzene-polymer network densities.

other hand, the carbonyl bands at around 1723  $\text{cm}^{-1}$  which are only due to the network, show no noticeable dichroism. This suggests that although azobenzene groups are aligned by the irradiation, the rest of the polymer network remains essentially disordered.

The macroscopic orientation of E7 resulting from light irradiation was measured from the CN band for the three E7/network samples. The results are shown in Figure 4, where the order parameters, which were calculated with respect to the molecular orientation direction, are plotted as a function of irradiation time. The following observations can be made. First, in all cases, an orientation of E7 is induced after 1–2 min of irradiation, but the duration of irradiation does have an effect on the achieved orientation level, which increases with time. For irradiation longer than 10 min, only small improvement of orientation can be obtained. Second, the level of the achievable orientation is sensitive to the concentration of azobenzene groups on the polymer network.  $S$  increases from  $\sim 0.07$  to  $\sim 0.28$  when the network concentration raises from 5% to 20%. On one hand, the need of a finite time (in minutes) for liquid crystal molecules to reach an appreciable orientation is understandable. What is measured here is the reaction of E7 molecules to the orientation of azobenzene groups. The orientation of azobenzene upon irradiation can be fast (in seconds in ref 4, for example), but the reaction of E7 involves changes in the director fields and evolution of defects, and this can need more time. Actually as compared with surface alignment, the orientation

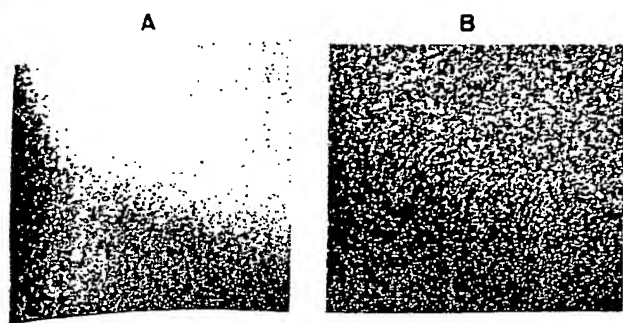


Figure 5. Polarized optical micrographs (125 $\times$ ) for an E7/network-90/10 film after 20 min irradiation at room temperature (A) and then heated to 53  $^{\circ}$ C (B). The film was placed with the UV polarization 45 $^{\circ}$  to crossed-polarizers.

development in Figure 4 is fast. On the other hand, the effects of network concentration on the orientation of E7 can be explained by the mole ratio of azobenzene to E7 molecules (Table 1). Qualitatively speaking, when an azobenzene group is aligned, liquid crystal molecules immediately surrounding this azobenzene should react first. Those first reactions activate cooperatively the orientation of other liquid crystal molecules more distant from the azobenzene unit, but this propagating effect should diminish with distance. A higher network density means less liquid crystal molecules to be activated per azobenzene group, and the aligning ability should be greater.

The induction of a macroscopic orientation of liquid crystal molecules in films of E7/network leads to changes in birefringence. An example is given in Figure 5. The photomicrographs were taken on an E7/network-90/10 film irradiated for 20 min. When the film was placed with the UV polarization direction making an angle of 45 $^{\circ}$  with respect to crossed-polarizers, the irradiated zone appeared bright as compared to the rest of the film, due to the orientation of E7 molecules. Heating the irradiated film, the birefringence was retained even at 53  $^{\circ}$ C, which was only 1  $^{\circ}$ C below  $T_{ni}$ . The lower birefringence in the vicinity of phase transition is indicative of a reduced macroscopic orientation of E7 due to thermal fluctuations. Not shown in Figure 5 is that when crossed-polarizers were rotated by 45 $^{\circ}$ , the contrast was reversed: the irradiated zone became slightly darker than the rest of the film.

Choosing the polarization of UV irradiation can control the orientation direction of E7 molecules in the irradiated zone. To illustrate such an orientation control, a performed experiment is depicted in Figure 6. A film of E7/network-90/10 was first irradiated; the absorbance of the CN band of the film was measured with a polarized IR beam, as a function of the angle between the UV and IR polarization directions. As expected, because of the liquid crystal orientation perpendicular to the UV polarization, the absorbance has a maximum value at 90 $^{\circ}$ . A second irradiation was then applied to the same film, rotating the UV polarization by 90 $^{\circ}$ . Under this transversal irradiation, azobenzene groups on the network should undergo a reorientation of 90 $^{\circ}$  and, as a result, reaction of E7 molecules should follow suit, again, take a longer time. Indeed, as can be seen from Figure 6, after 5 min transversal irradiation, the macroscopic orientation of E7 disappeared, with the CN absorbance showing no angular dependence. As the transversal irradiation goes on, reorientation of E7 molecules develops. After 40 min, the CN absorbance shows a minimum value at 90 $^{\circ}$ , indicating that the

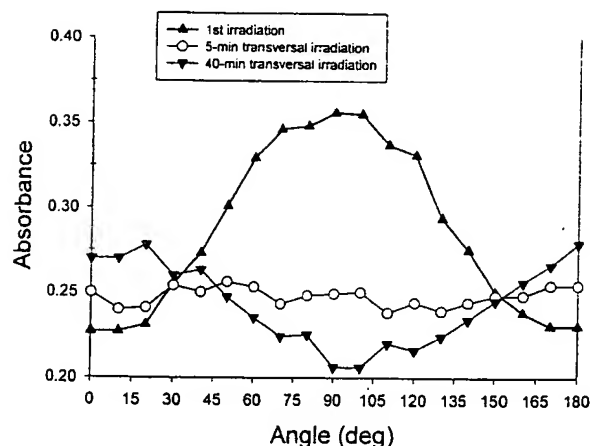


Figure 6. Angular dependence of infrared absorbance of cyano groups of E7 for an irradiated E7/network-90/10 film, the angle being that between the polarization of the infrared beam and the polarization of the first UV irradiation.

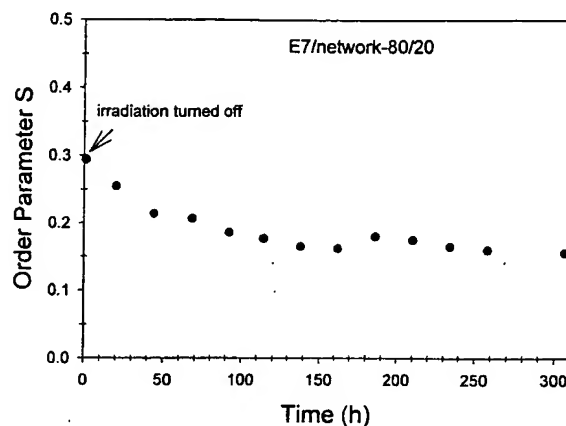


Figure 7. Order parameter of E7 at room temperature for an irradiated E7/network-80/20 film vs time after turning off the irradiation.

orientation of E7 molecules has changed direction by 90 $^{\circ}$ .

After the irradiation was turned off, the stability of the induced liquid crystal orientation at room temperature was examined. Generally, the orientation decayed during the first days following the irradiation, and then the relaxation was slowed down and the orientation was retained at an almost constant level. An example of the measurements made on the E7/network-80/20 is given in Figure 7. The order parameter  $S$  decreased gradually from  $\sim 0.3$  to  $\sim 0.17$  after about 4 days. Then, the remaining orientation became stable, showing little change with time. What is important to emphasize is that this stable liquid crystal orientation can only be held by the azobenzene-polymer network. When mixtures of E7/monomer were irradiated before polymerization, similar alignment of azobenzene molecules should occur, but immediately after the irradiation was turned off, IR measurements at room temperature showed no macroscopic orientation of E7 induced in the materials. Therefore, in the absence of a polymer network structure, the orientation relaxation of the azobenzene monomer must be fast. In the case of the E7/network, as the alignment of azobenzene groups could not be monitored through IR or UV dichroism, we do not know whether aligned azobenzene groups on the network are relaxed after turning off the irradiation. But there are two possibilities that can explain the



remaining liquid crystal orientation. (1) The relaxation of aligned azobenzene groups on the network is not complete, and the retained network anisotropy holds the orientation of E7 molecules. (2) Aligned azobenzene groups relax completely, but as the relaxation goes slowly, oriented liquid crystal molecules and defects have time to evolve. In the end, elastic free energies related to macroscopic orientation are released due to, for example, elimination of defects and the orientation becomes stable even without alignment of azobenzene groups.

Investigations were also made in thermal stability of the induced orientation of E7. When irradiated films were heated to temperatures above  $T_m$  of E7 and cooled back slowly to ambient, a macroscopic orientation was recovered, but only partially. Typically,  $S \sim 0.07$  was found following isotropization of E7 at  $T_m < T < 80^\circ\text{C}$ . When films were heated to  $T > 80^\circ\text{C}$ , they showed no orientation at all at room temperature. It seems that some alignment of azobenzene groups on the network could be preserved for treatments at  $T < 80^\circ\text{C}$  and that the oriented azobenzene could still impose some orientation to E7 while entering the nematic phase. Actually, even if azobenzene alignment remained intact, this partial orientation recovery of E7 was no surprise because of a different aligning mechanism involved. When irradiated at room temperature, nematic E7 molecules respond to the shearing movement of the azobenzene groups, whereas when cooled from the isotropic state, E7 molecules form a nematic phase under the effects of existing aligned azobenzene groups. As revealed by IR dichroism (Figure 3), the azobenzene moieties are aligned upon irradiation, but the remainder of the network is essentially disordered. In other words, the anisotropy of the network is limited to rigid azobenzene cores. This oriented network is different from that induced by a mechanical shearing or even that resulting from polymerization in oriented liquid crystals.<sup>1</sup> This explains the limited orientation recovery of E7 after isotropization.

## Conclusion

The synthesis of a diacrylate monomer containing an azobenzene group as its central core is shown. Thermal polymerization of the monomer dissolved in nematic liquid crystal E7 can result in a homogeneous azobenzene-containing polymer network that stabilizes the liquid crystal. When linearly polarized UV irradiation is applied on thin films of these materials, as a result of the alignment of azobenzene groups, a macroscopic molecular orientation of E7 can be induced perpendicular to the UV polarization direction. The liquid crystal orientation is achieved within minutes of irradiation at room temperature, and a significant degree of the induced orientation remains stable after turning off the

irradiation. The orientation level increases with increasing the polymer network density. However, the relatively low liquid crystal orientation could be indicative of the absence of a true molecular azobenzene network in the samples due to the employed thermal polymerization. The method presented in this paper represents a new means to control and manipulate the average orientation of liquid crystal molecules in materials such as PSLC. Liquid crystal molecules can be oriented in selected areas, and their orientation direction can be controlled.

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# New Development in Alignment Layers for Active Matrix TN-LCDs

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## Abstract

Synthesis, characterizations, and liquid crystal (LC) aligning capability of polyimide for the active matrix twisted nematic (AM-TN) LCD application are demonstrated and discussed. The synthesized PI materials in this research are featured by: 1) a low curing temperature (say, at 180 °C) due to their organic solvent soluble property; 2) a useful capability for a good unidirectional LC alignment; 3) a useful capability for generating a desired pretilt angle; and 4) an excellent voltage holding ratio. Discussions on the methods and mechanisms of the unidirectional LC orientation, the generation of pretilt angle, and the voltage holding ratio are made. The techniques of dividing each subpixel of a multi-color AM-TN-LCD into four parts, in which the surface LC directors of the adjacent parts are orthogonally directed to each other (called super-multidomain) or dividing a subpixel into a few thousands domains (called amorphous TN) are shown to be quite useful to improve the viewing angle and the gray scale characteristics of TN-LCDs. The surface LC alignment in these new techniques is also discussed by referring to non-rubbed polyimide and UV photo-curable polymer films.

## 1. Introduction

AM-TN-LCDs are being mass produced as useful flat panel display for various information equipments, such as computers, TVs and so forth. For manufacturing AM-TN-LCD devices, it is generally necessary to use liquid crystal (LC) orientation layers. Standard LC orientation layers that are commonly utilized for various LCDs are rubbed polyimide (PI) films.[1,2,3,4] The present review represents the discussion and demonstration of the synthesis, the characterizations, and the LC aligning capability of polyimide films for the current AM-TN-LCD application. The methods to obtain unidirectional orientation of LC molecules, generation of pretilt angle, and voltage holding ratio are discussed. The mechanisms of these phenomena are also discussed. In a previous paper, the author's research group reported that

**Table 1** Requirements for LC alignment films for AM-TN-LCDs application and concrete solutions.

Required properties	Concrete Solutions
Good Alignment of LCs	• Linear Polymer
Thermal stability (stable over 200 °C)	• Polyimides, Polyamides
Printability (film thickness: 5 ~ 10 nm)	• High viscosity • Addition of cellosolves
Low baking temperature (lower than 200 °C)	• Soluble Polyimides and Polyamides • Addition of imization accelerator (polyamic acid) • Polyamic acid with low T <sub>g</sub>
High voltage holding ratio (Higher than 95% at RT, higher than 90% at 60 °C)	• High purity monomer • Low polarity structure
High pretilt angle (2 ~ 4° for fluorescent LCs)	• Introduction of alkyl and fluorine groups • Other modification of polymer
Low residual DC (V <sub>offset</sub> lower than 0.1V)	• ?

the above-mentioned quartered division of each subpixel and amorphous TN are effective to improve the viewing angle characteristics of multi-color AM-TN-LCDs.[5,6,7] Besides the developed rubbed PI, the subject of other new polymers, such as non-rubbed PI and polarized UV light irradiated polymers as useful for the multidomain technology will also be discussed.

## 2. General requirements for LC orientation layers

Table 1 summarizes the requirements for LC orientation layers mainly for AM-TN-LCD application and solutions to related problems. This table was tabulated by collecting requirements and answers prepared by people who are engaged in this research field.[1,2,3]

## 3. Synthesis of polyimide materials

A precursor of polyimide can be typically synthesized by reacting an anhydride with a diamine; and the synthesized precursor is then polyimidized chemically or thermally. An organic solvent soluble PI for AM-TN-LCD application designated as Optomer AL1051 (JSR) is synthesized by reacting TCA AH (2,3,5-tricarboxycyclopentyl acetic dianhydride) and DDM (4,4'-

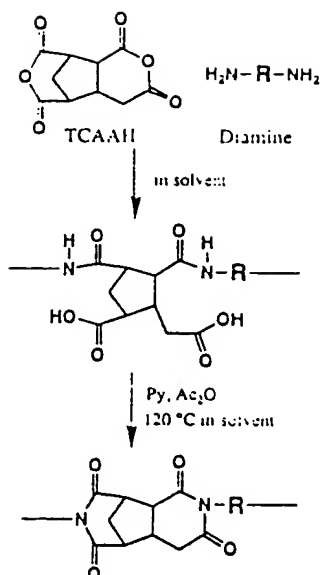


Fig.1 A reaction scheme of an organic-solvent soluble polyimide

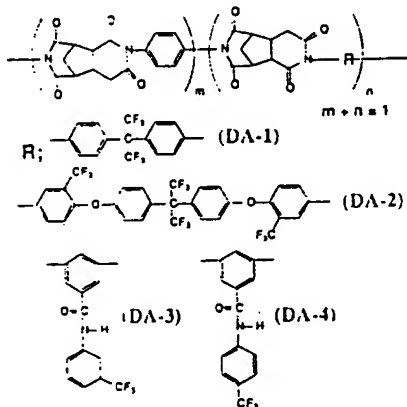


Fig.2 Chemical structure of polyimides containing fluorine atoms

Table 2 Anchoring Energies of various alignment Films for 5CB at 30 °C

<b>I. Polar Anchoring Energy</b>	
$A_0 > 10^{-3} \text{ J/m}^2$ (strong $\approx \infty$ )	Rubbed Polyimide
$A_0 \sim 10^{-4} \text{ J/m}^2$ (medium)	Rubbed Polypyrrole, Rubbed Polystyrene
$A_0 < 10^{-5} \text{ J/m}^2$ (weak)	PI-LB, Memory Effect of PI, 60° SiO
<b>II. Azimuthal Anchoring Energy</b>	
$A_\phi > 10^{-4} \text{ J/m}^2$ (strong $\approx \infty$ )	Rubbed Polyimide
$A_\phi > 10^{-5} \text{ J/m}^2$ (medium)	PI-LB, 60° SiO
$A_\phi > 10^{-6} \text{ J/m}^2$ (weak)	

angle from 5 degrees up to 27 degrees.[9,10] In this report our discussion concentrates mainly on the 2nd type (helical PIs with  $\text{CF}_3$ ) which is useful for manufacturing color AM-TN-LCDs.[1,2,3]

#### 4. Preparation of orientation films

The PI LC orientation layers are coated on ITO-deposited substrate plates and then cured. Conventionally, the cured PI films are mechanically rubbed to obtain a unidirectional LC alignment.[1,2,3,4]

#### 5. Characterizations of the aligned phase of nematic liquid crystals

##### 5.1 Texture

The aligned phase of a NLC medium in a TN-LCD can be evaluated and characterized by observing its texture with naked eye or with a microscope. A polarizing microscope is also useful to observe the conoscopic patterns.

##### 5.2 Image quality

The values, such as luminance contrast ratios and their contours (viewing angle), uniformity, gray scale capability, flickering, image sticking, crosstalk that determine the image quality of LCDs, more or less depend on the surface LC Alignment. The defects appearing in an improperly fabricated TN-LCD are reverse tilt and reverse twist disclinations. A defect free TN-LCDs can be fabricated 1) by giving appropriate pretilt angles and their senses; 2) by twist below 90 degrees (say, 87 degrees); and 3) by doping a chiral agent.[14,15] The existence of the appropriate surface pretilt angles removes the creation of the reverse tilt disclination, and the

aminodiphenylmethane) at 60 °C for 12 hours. Then the precursor, a synthesized polyamic acid, is polymerized at 120 °C for 3 hours in the presence of pyridine and acetic anhydride.[1,2] An example of the reaction scheme of an organic solvent soluble PI and its chemical structure with various moieties having  $\text{CF}_3$  are shown in Figs.1 and 2.

Various PI materials with different chemical structures have been developed for generating pretilt angles such as the follows: 1) PIs having alkyl branch terminals.[3,4,8,9,10]; 2) PIs having  $\text{CF}_3$  moieties with helical backbones and a zig-zag shape after rubbing.[11,12]; 3) PI having alkyl group in the main chain.[13]; The PI of type 1) having alkyl branches was prepared to fabricate STN-LCDs that need a high pretilt

methods 2) and 3) are effective to remove the reverse twist disclinations.[14,15]

### 5.3 Anchoring energy

The anchoring energies for polar and azimuthal deformations are important parameters for designing and characterizing TN-LCDs. The measured values for an nematic LC of 5CB obtained by our group are shown in Table 2.[3,4] It is shown that the anchoring energies for TN-LCDs prepared by using rubbed PI films are very strong.

### 5.4 Electrooptic characteristics, dielectric properties, and switching current

The EO characteristics and the electric field dependence of dielectric properties of the aligned phase of LCs reflect the surface alignment.[3] The appearance of a hysteresis in a capacitance versus applied DC voltages is originated from the existence of a surface electric charge bilayer that degrade the voltage holding ratio. The observation of switching current for pulsed waveform is also useful to investigate the surface charge accumulation.[1,2]

### 5.5 Nonlinear optics of the surface aligned phase

The measurement of the second harmonic generation from the LC molecules adsorbed at polymer surfaces is useful to understand the surface alignment.[16,17,18]

### 5.6 Residual surface ordering of LC

In the case where the substrate surface has a unidirectional LC aligning capability, there exist a thin layer of aligned LC layer even at above the clearing point.[19] A typical example is rubbed PI. This is a way to evaluate the surface order parameter. The application of this technique to PI films is now underway and the results will be published elsewhere.

## 6. Characterizations of LC orientation films

To characterize the properties and the characteristics of the LC orientation films, which give a great influence on the performance of various LCDs, the following characterizations are made by observing or measuring: 1) surface morphology or topography with an AFM or an EM; 2) birefringence (anisotropy in refractive index); 3) anisotropy in the UV absorption spectrum; 4) surface energy (polar, non polar), and wetting properties; 5) NMR to evaluate the degree of the polyimidation; 6) electrical conductivity; 7) dielectric constant; 8) thickness; 9) atomic composition by ESCA; 10) anisotropic infrared spectra; and so forth.[3,4]

## 7. Mechanisms of unidirectional LC alignment on polymer surfaces

The physical properties of an alignment polymer

**Table 3** The relation between the nature of alignment films and direction of unidirectionally aligned LC molecules.

Direction of Grooves	Direction of Slow Axis	Direction of NLC	Examples	References
→	→	→	Rubbed PI	3,4,21
(Dipping Direction) →	→	→	As stacked PI-LB	3,21,22,23
→	→	→	Micro Grooves	3,27,28
Weak Rubbing →	↕	↗ ↘	PS	3,4
→	↕	↕	PS	31,32
(Dipping Direction) →	↕	→	PF	30

Legend : PS : polystyrene. PF : polyfumarate

surface become anisotropic by the following treatments or work: stretching;[20] mechanical rubbing;[3,4,21] Langmuir-Blodgett film deposition;[22,23] polarized UV light irradiation of a photopolymer;[24,25,26] microgroove formation;[27,28] and so forth.

We have investigated the LC alignment capability of not only rubbed PIs but also other polymers. The results are summarized in Table 3. Regarding the LC alignment, which clarified through our research are as follows: 1) Just the surface of the substrate molecular layer plays a role in orienting LC molecules (examples are PI-LB film and polyfumarate).[3,29,30] 2) When the grooves and the optical slow axis (or principal axis for UV absorption) coincide, both factors will play a role in orienting LC molecules to be parallel to these two directions (an example is rubbed PI).[3,21,23] 3) But when the optical axis is perpendicular to the grooves, then there occurs a competition between the two forces and the LC molecules eventually align parallel to optical axis for a strong rubbing (an example is rubbed polystyrene).[31,32] 4) In the case where the backbone of a polymer is covered by a thick alkyl chains, the surface alkyl chains play a role in orienting LC molecule parallel to these main chains, even though the backbone has an optical axis perpendicular to the backbone direction (an example is polyfumarate).[30] 5) The grooves formed on an optically isotropic material surface are capable of aligning LC molecules parallel to the grooves.[27,28] 6) LC molecules oriented parallel to the optical slow axis generated on the surface of the polarized UV irradiated polyvinylcinnamate films or dyed polyvinyl alcohol films.[24,25,26] In these cases the optical slow axis is perpendicular to the polarization of the UV light. 7) Once an ensemble of LC droplet or a



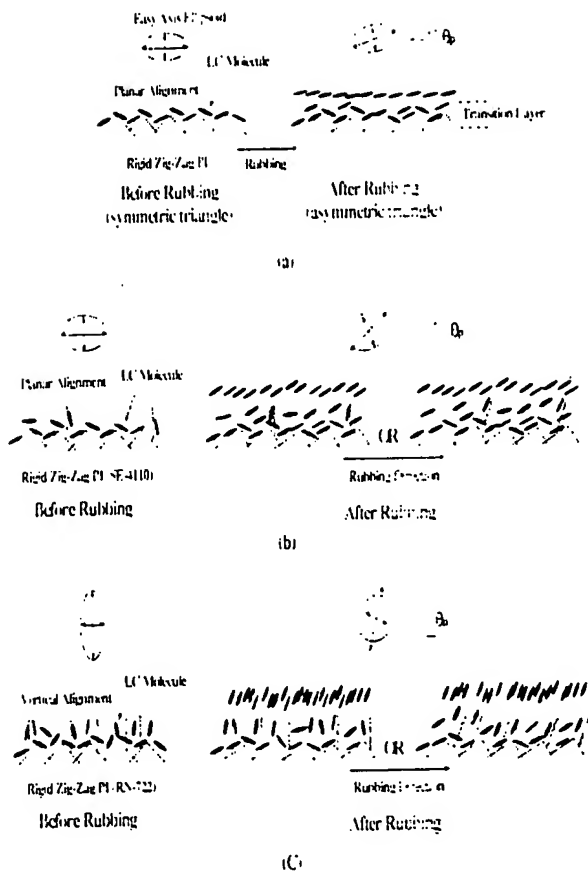


Fig.3 Schematic illustrations for explaining pretilt angle formation on various alignment films: (a) blanchless, (b) alkyl-blanchless (low density), and (c) alkyl-blanchless (high density) polyimides.

aligned LC medium, which has a finite LC order, contact with homogeneous (non rubbed) polymer surface (or on inorganic surface) then the LC molecules are immobilized and adhered. Examples are magnetically [33] or electrically [34] oriented LC or chiral NLC.[5,35] There occurs a finite LC ordering on these surfaces even above the clearing point of the NLC. Regarding models of the mechanism of unidirectional LC alignment on topographically and/or optically anisotropic substrates, several theories have been proposed: 1) groove theory [36] and 2) anisotropic VDW force.[37] According to the observations listed on Table 3, it may be claimed that both mechanisms work simultaneously or separately depending on the nature of surfaces; in the case where no grooves exist (e.g. LB films or hard PI), the anisotropic VDW force may play a major role in orienting LC molecules. Here, it is worthy to note that the anisotropic UV absorptions of both the substrate and the LC medium may be the major origin of the anisotropic VDW force.[37,38] For this reason, the characterization of an orientation

polymer film in terms of the birefringence, which are being used commonly, is done for reasons of convenience. In addition, it is generally not so easy to observe a very fine anisotropic topography induced by the polarized UV irradiation: This kind of observation is now underway.

### 8. Generation mechanism of surface pretilt angle

There is a so-called conical solution in the LC conformation in the free surface of NLCs or in a NLC aligned on a very nonpolar substrate.[39,40] However, it is not so easy to control the pretilt angle based on these theories. It is necessary to design and control the pretilt angle in the manufacturing of practical LCDs.[3]

According to research works including the author's group, it may be claimed that the surface pretilt angle can be generated by forming microscopic and asymmetric triangle structures formed on a substrate, where the size of these triangles are comparable to that of LC molecular length, and the steric interaction between LC molecules. These microscopic asymmetric triangles may play a role in determining the surface pretilt angle of the LC molecular conformation: the examples and evidences of this models are 1) obliquely evaporated SiO film, 2) rubbed PI having alkyl branches,[3,8,9,10] 3) rubbed PI

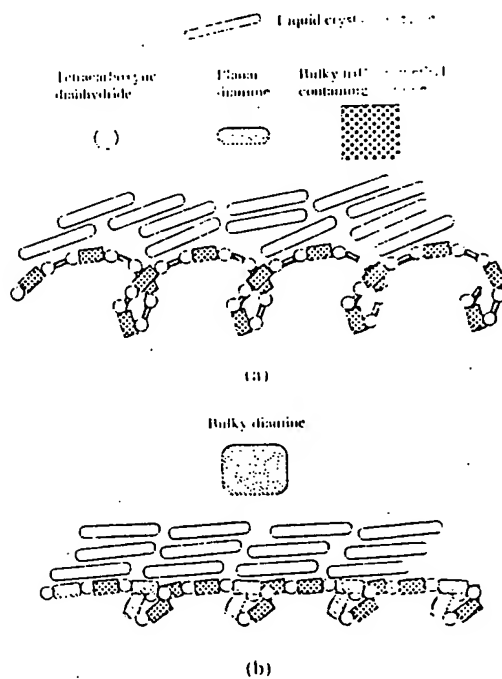


Fig.4 The role of the molecular shape of diamines in determining the surface molecular undulations. The planar diamine contributes to increase the undulation (Fig.4(a)) rather than the bulky diamine (Fig.4(b)). The PI(a) is capable of generating a higher pretilt angle about  $2.5^\circ$  than PI(b).

having helical backbone with  $\text{CF}_3$  moieties. [11,12] 4) PI-LB films with modified PI molecules, 5) microscopically fabricated triangles.[27,28] The application of an inhomogeneous electric field is also effective to form a tilted bulk LC conformation.

Fig.3 shows a model of the generation of surface pretilt angles in the case of 2) and 3). In particular, the type 3) is useful for AM-TN-LCDs and an illustrative model is shown in Fig.4: In this case the helices tend to form asymmetric triangles by rubbing. The shape of diamine determines the whole shape of the rubbed PIs. Concretely, plane diamine makes a larger contribution to increase the undulation of the PI (Fig.4(a)) than bulky diamine (Fig.4(b)). Actually, the former PI is capable of generating the pretilt angle of 3 degrees, while the latter is about 1 degree.

The dependence of the achieved pretilt angle on the chemical structures of PIs, which are useful for AM-TN-LCDs, is shown in Figs.5 and 6.

Generally, the pretilt angle decrease with increasing

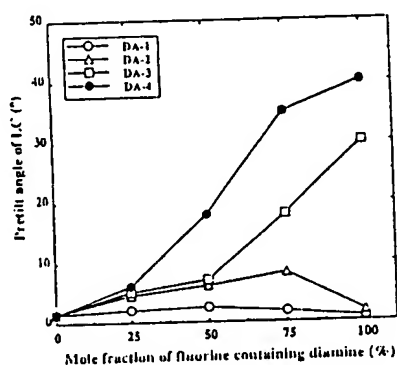


Fig.5 Relation between mole fraction of fluorine atoms containing diamines and pretilt angles of LC on polyimide films.

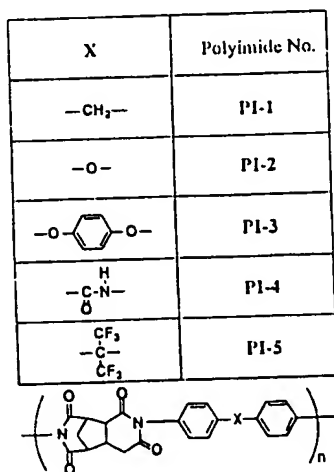


Fig.6 Chemical structures of polyimides.

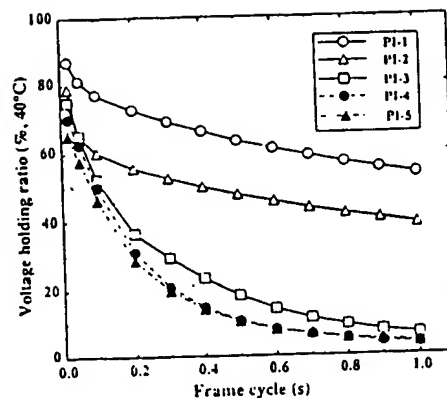


Fig.7 Voltage holding ratios of LC cells using solvent-soluble polyimides

temperature.[41,42] In projection display, the temperature of the LCD panel increases due to illumination; this causes the decrease of pretilt angle and creates disclinations. For this reason, it is necessary to give a high pretilt angle for projection use. However, in some cases a planar LC conformation tends to be homeotropic near the clearing point.[43] Regarding the LC material dependence of the pretilt angle, the pretilt angle depends on the dielectric constant (especially its perpendicular part) or birefringence of LC materials.[44,45] But these phenomenon strongly depends on the combination of the LC and substrate materials in a complicated way.

### 9. Voltage holding ratio

It is well known that the fluorinated NLCs show good voltage holding ratio, when they are used together with a special polyimide that is featured by nonpolarity.[1,46] The dependence of the voltage holding ratio on the PI materials is shown in Fig.7. The PIs such as PI-1 and -2 that contains  $-\text{CH}_2-$  or  $-\text{O}-$  group show a good voltage holding capability. It is shown that the nonpolar PI materials do not capture ions that form a depolarization field. It is claimed that the formation of the depolarization field may cause the degradation of the voltage holding ratio.

### 10. Improvement of the viewing angle characteristics of AM-LCD in terms of surface alignment

A conventional TN-LCD, which is fabricated using conventional rubbing technique exhibits a nonuniform viewing angle characteristic.[5] Therefore there is a strong demand for the improvement of the viewing angle characteristics. This improvement can be achieved by dividing each subpixel of a multi-color TN-LCD into two.

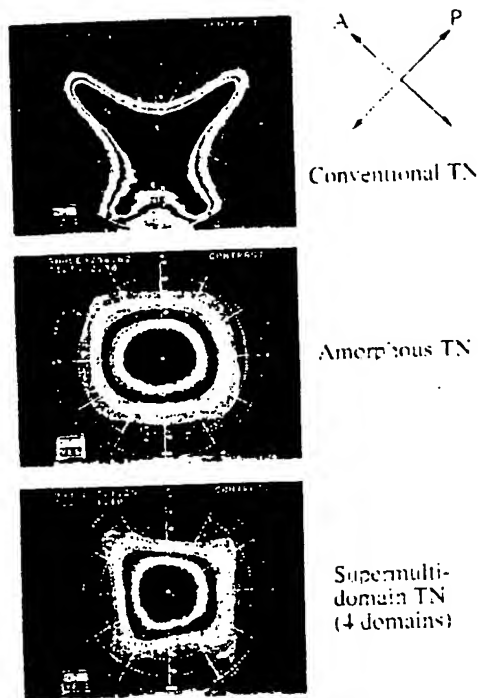


Fig.8 Iso-contrast curves for various display modes

four, all the way up to several thousand parts.[5,6,7] The latter case is called the amorphous TN-LCD.[5,6,7] According to Sugiyama et al., the best way is to divide each subpixel into four parts [6]; this technology is called the quartered subpixel or super-multidomain.[7] Fig.8 compares the iso-contrast ratio curves of the conventional, amorphous (a), and the quartered (SMD) TN-LCDs. The second and third ones show uniform viewing angle characteristics as much better than the conventional TN-LCD. A SMD-TN cell was fabricated by using polarized UV light irradiated polyvinylcinnamate with one mask.[7]

The new techniques called the polymer stabilized a- and SMD-TN-LCDs are useful to immobilize and freeze the reverse tilt disclinations. In this case, NLC is doped with a photo-diacrylic-polymer to give a bulk tilt angle even though no surface pretilt exists.[47] The experimental result of the viewing angle characteristic for a polymer-stabilized a-TN-LCDs is shown in Fig.9. From this result, it is clear that the homogeneous viewing angle characteristic is also obtained using this display mode.

### 11. Concluding remarks

The required characteristics for the polyimide LC alignment films in AM-LCD application, such as low temperature process (say, 180 °C) and the generation of pretilt angle, are empirically realized. However, in order to improve the viewing angle characteristics of multi-color

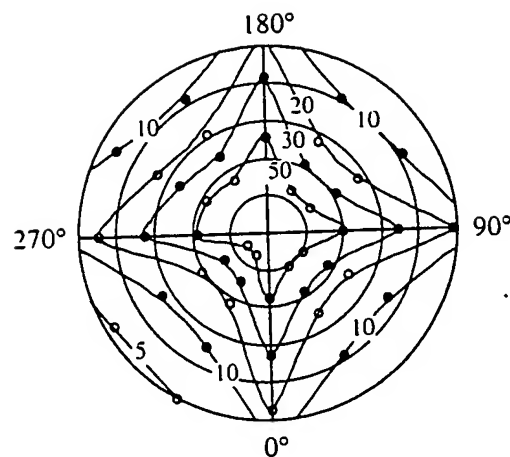


Fig.9 An iso-contrast curve of a polymer-stabilized a-TN-LCD

AM-LCDs it is necessary to develop a new technique for quartered subpixel (super-multidomain) by synthesizing new materials and developing new manufacturing processes. This research is now under way, and the results will be published elsewhere.

### Appendix Notes

Regarding the measuring methods of polar and azimuthal anchoring energies of planar nematic LC media, please refer to the references 48 and 49, respectively.

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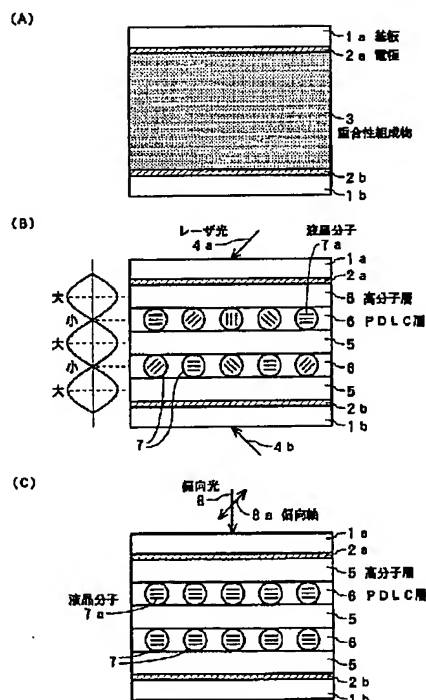
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(54) 【発明の名称】 高分子分散液晶素子およびその製造方法

(57) 【要約】

【課題】 高分子化合物と低分子液晶の複合構造で構成され、かつ内部で屈折率が周期的に変化する多層構造を有する P D L C 素子において、高い反射率が得られるようにする。

【解決手段】 セルに、少なくとも、ジアゾ色素分子側鎖を有する重合性化合物、低分子液晶および重合性基の重合開始剤を含む重合性組成物 3 を注入する。セルにレーザー光 4 a、4 b を照射して、重合性組成物 3 中においてレーザー光 4 a、4 b を干渉させる。レーザー干渉光の振幅が大きい領域では、重合性化合物が重合、硬化して、高分子層 5 が形成され、レーザー干渉光の振幅が小さい領域では、相分離を生じて、P D L C 層 6 が形成される。直線偏光の、偏向軸 8 a が基板面に平行な面内に存在する偏向光 8 をセルに照射する。これによって、液晶領域 7 と高分子領域の界面におけるジアゾ色素分子側鎖が、偏向光 8 の偏向軸 8 a に垂直な方向に屈曲し、これに沿って液晶領域 7 内の液晶分子 7 a が配向される。



【特許請求の範囲】

【請求項1】 高分子化合物と低分子液晶の複合構造で構成され、かつ内部で屈折率が周期的に変化する多層構造を有する高分子分散液晶素子において、前記高分子化合物が、直線偏光の照射によって所定方向に異性化したジアゾ色素分子側鎖を有し、前記低分子液晶が、その異性化したジアゾ色素分子側鎖によって所定方向に配向されていることを特徴とする高分子分散液晶素子。

【請求項2】 請求項1の高分子分散液晶素子において、前記多層構造は、高分子層と高分子分散液晶層とが交互に積層されたものであることを特徴とする高分子分散液晶素子。

【請求項3】 請求項1の高分子分散液晶素子において、前記多層構造は、前記異性化したジアゾ色素分子側鎖によって互いに低分子液晶の配向方向が直交するものとされた2種の高分子分散液晶層が交互に積層されたものであることを特徴とする高分子分散液晶素子。

【請求項4】 請求項1～3のいずれかの高分子分散液晶素子において、液晶領域のサイズが可視光の波長より小さいことを特徴とする高分子分散液晶素子。

【請求項5】 ジアゾ色素分子側鎖を有する重合性化合物と低分子液晶とを含む重合性組成物に、干渉波を照射して、前記重合性化合物を重合し、その後、直線偏光を照射して、前記ジアゾ色素分子側鎖を異性化し、これにより前記低分子液晶を配向させることを特徴とする液晶素子製造方法。

【請求項6】 ジアゾ色素分子側鎖を有する重合性化合物と低分子液晶とを含む重合性組成物に、熱を加え、または光を照射して、前記重合性化合物を重合し、その後、直線偏光を照射して、前記ジアゾ色素分子側鎖を異性化し、これにより前記低分子液晶を配向させるとともに、その後さらに、偏向軸が前記直線偏光の偏向軸と直交する光による干渉光を照射して、前記ジアゾ色素分子側鎖の一部を異性化し、これにより前記低分子液晶の一部の配向方向を他の部分の配向方向に対して直交させることを特徴とする液晶素子製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 この発明は、表示素子、調光素子、光変調素子などとして用いることができる高分子分散液晶素子およびその製造方法に関する。

【0002】

【従来の技術】 表示素子や調光素子として、3次元構造の高分子の空隙中に液晶を分散させた高分子分散液晶 (Polymer Dispersed Liquid Crystal) を用いた素子が知られている。以下、高分子分散液晶をPDLCと称し、高分子分散液晶素子もPDLC素子と称する。

【0003】 図8は、このPDLC素子の一例を示し、基板1a上の電極2aと基板1b上の電極2bとの間に、高分子領域15中に液晶領域 (液晶ドロブレット) 7が分散されたPDLC層16を形成したものである。

【0004】 このPDLC素子においては、電極2a, 2b間に電圧が印加されないとき、同図(A)に示すように、液晶領域7内の液晶分子7aがランダムな方向を向くことにより、液晶と高分子との間に屈折率の差を生じて、液晶と高分子との界面で入射光11が屈折し、PDLC層16全体では入射光11が多数の液晶領域7を通過することになって、散乱状態となる。

【0005】 電極2a, 2b間に電圧を印加すると、同図(B)に示すように、液晶領域7内の液晶分子7aが基板面に垂直に配向し、液晶分子7aの長軸方向の屈折率と高分子の屈折率とを等しくしておくことによって、PDLC層16は透明状態となり、入射光11は透過光13としてPDLC層16を透過する。

【0006】 この高分子分散液晶素子は、偏光板が不要であるので、明るい表示が期待され、プロジェクタライトバルブなどへの応用が考えられている。

【0007】 高分子と液晶の複合構造としては、液晶が分布する領域が互いに独立に存在したものや、液晶が連続的に分布したもの、などが考えられているが、このような高分子液晶複合膜の製造方法としては、大きく分けて、以下の3つが提案されている。

【0008】 第1は、液晶をランダムに配向させることができる多孔質ポリマーに液晶を含浸させる方法である。第2は、溶媒にポリマーと液晶を混合して乳化させた後、溶媒を蒸発させることによって、ポリマーを硬化させる方法である。第3は、モノマーやオリゴマー、またはそれらの混合物と液晶を混合した重合性組成物に、熱を加え、または紫外線などを照射することによって、ポリマーを重合させるとともに、ポリマーと液晶を相分離させる方法である。

【0009】 また、このPDLCの他の例として、SPIE. 1080, 83, (1989) には、内部で屈折率が周期的に変化するPDLC素子が示されている。

【0010】 具体的には、図9に示すように、基板1a上の電極2aと基板1b上の電極2bとの間に、主として高分子からなる高分子層18と、高分子領域中に液晶領域7が分散されたPDLC層19とを、交互に多層に渡って積層して、屈折率の周期的な変化の構造を形成したものである。

【0011】 このPDLC素子においては、電極2a, 2b間に電圧が印加されないとき、高分子層18とPDLC層19とによる屈折率の周期的な変化によって、干渉フィルタの原理により、同図(A)に示すように、入射光11中の特定波長成分を反射光12として反射させる。

【0012】電極2a, 2b間に電圧を印加すると、同図(B)に示すように、液晶領域7内の液晶分子7aが基板面に垂直に配向され、液晶分子7aの長軸方向の屈折率と高分子の屈折率とを等しくしておくことによって、高分子層18とPDL層19とによる屈折率の周期的な変化が消失して、入射光11は大部分が透過光13としてセルを透過する。

【0013】

【発明が解決しようとする課題】図9のPDL素子は、干渉フィルタの原理によって、高い反射率が得られ、明るい表示が得られることが、期待される。

【0014】しかしながら、図9のPDL素子では、電極2a, 2b間に電圧が印加されないとき、液晶領域7内の液晶分子7aはランダムな方向を向いているので、高分子層18とPDL層19との間の屈折率差が小さく、実際上は、高い反射率が得られない。

【0015】すなわち、このとき、液晶領域7内の液晶分子7aの配向は、PDL層19全体ではランダムとなるので、PDL層19の屈折率 $n_a$ は、液晶領域7の一次近似された屈折率 $(n_e + 2n_o)/3$ 、PDL層19中の高分子の屈折率 $n_p$ 、PDL層19中の液晶の高分子に対する体積分率 $v$ から、

$$n_a = \{n_o(3-v) + n_e\} / 3 \quad \cdots (1)$$

で表される低い値となる。ただし、 $n_e$ は液晶の異常光に対する屈折率、 $n_o$ は液晶の通常光に対する屈折率である。

【0016】このため、高分子層18とPDL層19との間の屈折率差が小さく、高い反射率が得られない。

【0017】図9のPDL素子のように、PDLとして高分子と液晶の複合構造で構成され、しかも内部で屈折率が周期的に変化する多層構造を有する液晶素子において、内部の液晶を特定方向に配向させることができれば、高分子層とPDL層との間の屈折率差、ないし内部の周期的な屈折率の変化を大きくすることができ、高い反射率を得ることができる。

【0018】PDL素子では、以下に示すように、初期状態における液晶の配向方向を制御することが考えられている。

【0019】(1) 米国特許第5, 188, 760号明細書には、PDLの前駆体である重合性組成物に液晶性モノマーを用いて、配向膜付きセルに注入し、紫外線や熱を加えることによって、液晶性モノマーの重合体である液晶性高分子と低分子液晶とを、配向膜の方向に配向した状態で重合相分離し、液晶性モノマー硬化後には低分子液晶の配向が固定されるようにする方法が示されている。

【0020】(2) 特開平5-281527号には、重合性組成物を配向膜のないセル内に注入し、セルに対して水平方向に外部から磁場や電場を印加した状態で、紫外線や熱を加えることによって、低分子液晶が外場の方

向に配向した状態で重合相分離を行い、重合性組成物硬化後には低分子液晶の配向が固定されるようにする方法が示されている。

【0021】(3) 「Japan Display' 92. 699」には、PDLの前駆体である重合性組成物を、液晶濃度が非常に高い液晶相となるように調製して、配向膜付きセルに注入し（この状態では液晶相状態の重合性組成物は配向膜の方向に配向している）、紫外線や熱を加えて重合相分離させることによって、低分子液晶の配向を初期配向状態のまま固定する方法が示されている。

【0022】(4) 「Mol. Mat., 2, 295 (1993)」には、まず、乳化法によって、ジアゾ色素分子側鎖を有する高分子化合物と、その高分子化合物の貧溶媒からなる複合膜を作製し、次に、この複合膜から貧溶媒を抽出し、複合膜を乾燥させて、ジアゾ色素分子側鎖を有する高分子化合物からなる多孔質ポリマーを作製し、次に、この多孔質ポリマーに低分子液晶を含浸させて、ジアゾ色素分子側鎖を有する高分子化合物からなるPDLを作製し、次に、このPDLに偏光を照射して光2量化反応を生じさせ、この光2量化反応による高分子化合物の構造変化に伴って、低分子液晶を配向させる方法が示されている。

【0023】しかしながら、(1)(3)の方法では、配向膜によって液晶を配向制御するので、図9に示すような、内部で屈折率が周期的に変化する多層構造を形成することができない。

【0024】また、(2)の方法では、セルと平行に磁場または電場を印加するので、セルサイズが大きい場合には、セルの全面に渡って有効な外場を印加することが困難となる。例えば、特開平5-281527号には、外部電場を印加する場合には電場の大きさが1kV/cm以上は必要であると記載されている。しかし、対角12インチのセルサイズを仮定すると、印加電圧は約350kV以上必要となる計算になり、このように大きな印加電圧は容易には実現できない。

【0025】さらに、(4)の方法では、含浸法でしか素子を作製することができない。しかし、含浸法では、図9に示すような、内部で屈折率が周期的に変化する多層構造を形成することはできない。

【0026】要するに、従来の方法では、高分子化合物と低分子液晶の複合構造で構成され、かつ内部で屈折率が周期的に変化する多層構造を有するPDL素子において、高い反射率を得ることはできない。

【0027】そこで、この発明は、高分子化合物と低分子液晶の複合構造で構成され、かつ内部で屈折率が周期的に変化する多層構造を有するPDL素子において、高い反射率が得られ、明るい表示が得られるようにしたものである。

【0028】



【課題を解決するための手段】この発明の高分子分散液晶素子は、高分子化合物と低分子液晶の複合構造で構成され、かつ内部で屈折率が周期的に変化する多層構造を有する高分子分散液晶素子において、前記高分子化合物は、直線偏光の照射によって所定方向に異性化したジアゾ色素分子側鎖を有するものとし、前記低分子液晶は、その異性化したジアゾ色素分子側鎖によって所定方向に配向されているものとする。

【0029】

【作用】ジアゾ色素分子側鎖は、これに直線偏光した可視光を照射することによって、その偏光軸に垂直な方向に分子が折れ曲がったシス構造に異性化する性質を有する。

【0030】したがって、高分子化合物と低分子液晶の複合構造で構成され、かつ内部で屈折率が周期的に変化する多層構造を有する高分子分散液晶素子において、その高分子化合物をジアゾ色素分子側鎖を有するものとして、高分子分散液晶素子に直線偏光を照射することによって、高分子化合物中のジアゾ色素分子側鎖が偏光の偏光軸に垂直な所定方向に異性化し、これにより液晶領域内の液晶分子も所定方向に配向される。

【0031】この発明では、このような原理に基づいて、高分子化合物と低分子液晶の複合構造で構成され、かつ内部で屈折率が周期的に変化する多層構造を有する高分子分散液晶素子において、高分子化合物が、直線偏光の照射によって所定方向に異性化したジアゾ色素分子側鎖を有し、低分子液晶が、その異性化したジアゾ色素分子側鎖によって所定方向に配向されているものとする。

【0032】したがって、この発明の高分子分散液晶素子においては、これに電界や磁界などが印加されない初期状態において、高分子領域中に分散された液晶領域中の液晶分子が、ランダムな方向ではなく、所定方向を向くようになり、内部の周期的な屈折率の変化を大きくすることができ、高い反射率を得ることができるようになる。

【0033】

【発明の実施の形態】【第1の実施形態】図1は、この発明の製造方法の第1の例を示し、図2は、これによって得られる、この発明のPDLC素子の第1の例を示す。

【0034】まず、図1(A)に示すように、一面側に電極2aが形成された基板1aと、一面側に電極2bが形成された基板1bとを、電極2a、2bを内側にして所定間隔で対向させて、セルを形成する。基板1a、1bおよび電極2a、2bは、光透過性を有するものとする。

【0035】次に、このセルに重合性組成物3を注入する。重合性組成物3は、少なくとも、ジアゾ色素分子側鎖を有する重合性化合物、低分子液晶および重合性基の

重合開始剤を混合して、調製する。

【0036】ジアゾ色素分子側鎖を有する重合性化合物は、ジアゾ色素分子側鎖を持った化合物に、重合性基であるアクリロイル基やメタクロイル基を付与した化合物、およびその誘導体である。

【0037】ジアゾ色素分子としては、これを含む高分子を配向膜として用いた場合に、トランス体において、液晶を基板面と平行な方向に配向させるプレーナ配向の性質を持ち、さらに色素が吸収する波長の直線偏光の照射によって、その偏光軸と直交する方向に液晶を配向させる性質を有するものを用いる。このような性質を有するジアゾ色素重合体としては、例えば、図5(A)

(B) (C)に示すような分子を用いることができる。

【0038】重合性組成物は、少なくともジアゾ色素分子側鎖を有する重合性組成物を含むものとするが、その以外にも種々の重合性組成物を組み合わせて使用して、ポリマーの骨格を形成することができる。例えば、アクリル酸アルキルエステル、アクリルアミド、アクリル酸ヒドロキシエステル、メタクリル酸アルキルエステル、メタクリルアミド、メタクリル酸ヒドロキシエステル、ビニルピロリドン、スチレンおよびその誘導体、アクリロニトリル、塩化ビニル、塩化ビニリデン、エチレン、ブタジエン、イソプレン、ビニルピリジンなどの、単官能および多官能モノマーが好ましく、特に粘度が高いものが好適である。

【0039】重合性組成物には、重合性化合物を重合させるために、可視光もしくは紫外光または熱による重合開始剤を含める。

【0040】低分子液晶としては、ネマチック液晶、コレステリック液晶、スメクチック液晶、および強誘電性液晶など、一般的に電界駆動型表示材料として用いられている種々の低分子液晶材料を用いることができる。具体的には、ビフェニル系、フェニルベンゾエート系、シクロヘキシルベンゼン系、アゾキシベンゼン系、アゾベンゼン系、ターフェニル系、ビフェニルベンゾエート系、シクロヘキシルビフェニル系、フェニルピリミジン系、シクロヘキシルピリミジン系などの各種低分子液晶化合物を用いることができる。これらの低分子液晶化合物は、一般に使用されている低分子液晶材料と同様に、単一の組成である必要はなく、複数の成分から構成される化合物でもよい。

【0041】次に、図1(B)に示すように、基板1aおよび1bの外側からセルに、レーザ光4aおよび4bを照射して、重合性組成物3中において、レーザ光4aおよび4bを干渉させる。

【0042】これによって、レーザ干渉光の振幅が大きい領域では、重合性化合物が重合、硬化して、屈折率の低い高分子層5が形成されるとともに、レーザ干渉光の振幅が小さい領域では、相分離を生じて、液晶領域7を有する屈折率の高いPDLC層6が形成される。レーザ

干渉光の振幅が大きい領域と小さい領域は、空間的に交互に繰り返されるので、屈折率が周期的に変化するPDL C素子が作製されることになる。ただし、この段階では、PDL C層6中の液晶領域7内の液晶分子7aはランダムな方向に配向されている。

【0043】次に、図1(C)に示すように、一方の基板1aの外側からセルに、偏向光8を照射する。偏向光8は、直線偏光の、偏向軸8aが基板面に平行な面内に存在する平面波として、基板面に垂直に照射する。

【0044】これによって、それぞれのPDL C層6においては、液晶領域7と高分子領域の界面におけるジアゾ色素分子側鎖が、基板面に平行な面内において、偏向光8の偏向軸8aに垂直な方向に屈曲し、これに沿って、液晶領域7内の液晶分子7aが配向されるようになる。

【0045】したがって、偏向光8の照射後のPDL C素子は、電極2a、2b間に電圧が印加されない初期状態において、PDL C層6内の液晶分子7aが全て、基板面に平行な面内において所定方向に配向され、高分子層5とPDL C層6との間の屈折率差が大きくなって、高い反射率が得られるようになり、図2(A)に示すように、入射光11中の特定波長成分を反射光12として、高い反射率で反射させる。

【0046】電極2a、2b間に電圧を印加すると、同図(B)に示すように、PDL C層6内の液晶分子7aが全て、基板面に垂直に配向され、液晶分子7aの長軸方向の屈折率と高分子の屈折率とを等しくしておくことによって、高分子層5とPDL C層6とによる屈折率の周期的な変化が消失して、入射光11は大部分が透過光13としてセルを透過する。

【0047】なお、偏向光8の波長は、ジアゾ色素分子側鎖によって異なるが、450nm前後のものをを用いることができる。照射時間は、光の強度やジアゾ色素分子側鎖の感度などによっても異なるが、1分～120分程度とするのが望ましい。

【0048】液晶領域7は、異性化したジアゾ色素分子側鎖によって内部の液晶分子7aを確実に配向させるためには、できるだけ小さい方が望ましい。具体的には、可視光の波長より小さいサイズとする。

【0049】このように液晶領域7を小さくする方法としては、重合性組成物の粘度を高め、また多官能アクリルモノマーのような重合速度の速いものを用いるなどの方法をとることができる。

【0050】〔第2の実施形態〕図3は、この発明の製造方法の第2の例を示し、図4は、これによって得られる、この発明のPDL C素子の第2の例を示す。

【0051】まず、基板1a、1bを、電極2a、2bを内側にして所定間隔で対向させて、セルを形成する。次に、このセルに、図1の例と同様に、ジアゾ色素分子側鎖を有する重合性化合物、低分子液晶および重合性基

の重合開始剤を混合して調製した重合性組成物を注入する。

【0052】次に、図3(A)に示すように、この重合性組成物が注入されたセルに紫外線9を照射して、重合性化合物を重合、硬化させることによって、高分子領域中に液晶領域7が分散されたPDL C層10を形成し、図8に示したようなPDL C素子を形成する。

【0053】この段階では、屈折率が周期的に変化する多層構造は形成されていないとともに、PDL C層10中の液晶領域7内の液晶分子7aはランダムな方向に配向されている。

【0054】次に、図3(B)に示すように、一方の基板1aの外側からセルに、偏向光8を照射する。偏向光8は、直線偏光の、偏向軸8aが基板面に平行な面内に存在する平面波として、基板面に垂直に照射する。

【0055】これによって、PDL C層10においては、液晶領域7と高分子領域の界面におけるジアゾ色素分子側鎖が、基板面に平行な面内において、偏向光8の偏向軸8aに垂直な方向に屈曲し、これに沿って、液晶領域7内の液晶分子7aが配向されるようになる。

【0056】したがって、偏向光8の照射後には、PDL C層10中の液晶分子7aは全て、基板面に平行な面内において所定方向に配向されるようになる。ただし、この段階でも、屈折率が周期的に変化する多層構造は形成されていない。

【0057】次に、図3(C)に示すように、基板1aおよび1bの外側からセルに、レーザー光4aおよび4bを照射して、PDL C層10中において、レーザー光4aおよび4bを干渉させる。ただし、この場合、レーザー光4aおよび4bは、それぞれ、図3(B)の工程において照射した偏向光8の偏向軸8aと直交する偏向軸を有するものとする。

【0058】これによって、レーザー干渉光の振幅が大きい領域10aでは、液晶領域7と高分子領域の界面におけるジアゾ色素分子側鎖が、基板面に平行な面内において、レーザー光4a、4bの偏向軸に垂直な方向に屈曲し、これに沿って、領域10aにおける液晶領域7内の液晶分子7aが、基板面に平行な面内において、もとの偏向光8の照射によって決定された方向に対して垂直な方向に配向される。レーザー干渉光の振幅が小さい領域10bでは、ジアゾ色素分子側鎖が異性化せず、したがって液晶領域7内の液晶分子7aの配向方向も変わらない。

【0059】そして、レーザー干渉光の振幅が大きい領域10aと小さい領域10bは、空間的に交互に繰り返されるので、図1および図2に示した例のように高分子層5とPDL C層6が交互に繰り返される形態ではなく、互いに液晶分子7aの配向方向が異なることにより屈折率が異なる2種のPDL C層10a、10bが交互に繰り返される形態の、屈折率が周期的に変化するPDL C

素子が作製されることになる。

【0060】この例のPDLC素子は、電極2a、2b間に電圧が印加されない初期状態において、屈折率の周期的な変化を形成する2種のPDLC層10a、10bが互いに直交する方向に配向された液晶によって構成されるので、屈折率の周期的な変化が大きくなって、高い反射率が得られるようになり、図4(A)に示すように、入射光11中の特定波長成分を反射光12として、高い反射率で反射させる。

【0061】電極2a、2b間に電圧を印加すると、同図(B)に示すように、PDLC層6内の液晶分子7aが全て、基板面に垂直に配向され、液晶分子7aの長軸方向の屈折率と高分子の屈折率とを等しくしておくことによって、高分子層5とPDLC層6とによる屈折率の周期的な変化が消失して、入射光11は大部分が透過光13としてセルを透過する。

【0062】〔他の実施形態〕この発明の製造方法としては、上述した方法のほかに、例えば、以下のような方法を行うこともできる。

【0063】まず、ジアゾ色素の末端に重合性官能基を有する重合性化合物、多官能アクリルモノマー、低分子液晶、および重合性基の重合開始剤を混合して、重合性組成物を調液し、セルに注入する。この場合、液晶領域7を小さくするために、アクリルモノマーは重合速度の速い多官能モノマーとし、混合された重合性組成物は粘度が高くなるようにする。

【0064】さらに、このセルに対してレーザー光による干渉光を照射する。レーザー干渉光の振幅が大きい領域では、レーザー光の偏向軸と垂直な方向に、液晶と高分子の界面のジアゾ色素分子側鎖が屈曲し、液晶はこれに従って配向する。レーザー干渉光の振幅が小さい領域では、配向方向はランダムなままとなる。レーザー干渉光の振幅の大きい領域と小さい領域は、空間的に交互に繰り返されるため、屈折率が周期的に変化するPDLC素子を作製することができる。

【0065】〔実施例〕この発明のPDLC素子を試し、その特性を測定した。

【0066】（実施例1）実施例1では、図1に示した例の方法によって、図2に示した例のPDLC素子を作製した。

【0067】ジアゾ色素モノマーとして、図5(A)のジアゾ色素モノマーを合成した。重合性化合物は、ジペンタエリスルトールヘキサアクリレート（日本化薬社製）80wt%、Nビニルピロリドン（和光純薬社製）20wt%とした。低分子液晶として、ネマチック液晶E7（メルク社製）を用いた。

【0068】ジアゾ色素10wt%、重合性化合物50wt%、液晶40wt%を混合し、重合性化合物の重合開始剤としてローズベンガル（和光純薬社製）5mMとN-フェニルグリシン（和光純薬社製）50mMとを添

加して、重合性組成物を調液した。

【0069】2枚のITO透明電極付き石英基板を10μmのギャップ間隔で貼り合わせたセルに、調液した重合性組成物を注入した。

【0070】488nmのArイオン・レーザー光を、ビームエキスパンダによりビーム径を拡大した後、2光束に分け、重合性組成物を注入したセルの表裏から、セル内に10分間照射して、内部で屈折率が周期的に変化する多層構造を有するPDLC素子を得た。

【0071】さらに、488nmのArイオン・レーザー光を、ビームエキスパンダによりビーム径を拡大して得た直線偏向光を、セルの片側からセル内に照射した。

【0072】（実施例2）実施例2では、図3に示した例の方法によって、図4に示した例のPDLC素子を作製した。

【0073】ジアゾ色素モノマー、重合性化合物および低分子液晶としては、実施例1と同じものを使用した。ジアゾ色素10wt%、重合性化合物50wt%、液晶40wt%を混合し、重合性化合物の重合開始剤としてダロキシア1173（日本チバガイギー社製）5wt%を添加して、重合性組成物を調液した。

【0074】2枚のITO透明電極付き石英基板を10μmのギャップ間隔で貼り合わせたセルに、調液した重合性組成物を注入した。

【0075】高圧水銀灯を光源とした50mWの紫外線を、重合性組成物を注入したセルの片側から、セル内に5分間照射して、PDLC素子を得た。

【0076】次に、488nmのArイオン・レーザー光を、ビームエキスパンダによりビーム径を拡大して得た直線偏向光を、セルの片側からセル内に照射した。

【0077】さらに、488nmのArイオン・レーザー光を、ビームエキスパンダによりビーム径を拡大した後、2光束に分け、セルの表裏からセル内に10分間照射して、内部で屈折率が周期的に変化する多層構造を有するPDLC素子を得た。

【0078】（反射特性の測定と評価）作製した試料の反射率は、図6に示すような、白色光が得られる光源31、ゴニオメーターヘッドを用いたθ-2θ光学系、およびスペクトロメータ34を組み合わせた評価用光学系30で測定した。すなわち、光源31からの白色光を入射光32として試料20の素子に入射させ、試料20からの反射光33をスペクトロメータ34で測定した。

【0079】図7に、測定評価の結果を示す。ここでは、体積ホログラム素子の反射率特性評価の目安として、反射率30%以下を「×」、30%~50%を「△」、50%~70%を「○」、70%以上を「☆」とした。

【0080】図7に示すように、この発明の方法ないし素子によれば、反射率が向上することがわかる。

【0081】

【発明の効果】 上述したように、発明によれば、高分子化合物と低分子液晶の複合構造で構成され、かつ内部で屈折率が周期的に変化する多層構造を有する高分子分散液晶素子において、反射率を高くすることができる。

【0082】 また、発明によれば、そのような高分子分散液晶素子を確実にかつ容易に得ることができる。

【図面の簡単な説明】

【図1】 この発明の製造方法の一例を示す図である。

【図2】 この発明の高分子分散液晶素子の一例を示す図である。

【図3】 この発明の製造方法の他の例を示す図である。

【図4】 この発明の高分子分散液晶素子の他の例を示す図である。

【図5】 ジアゾ色素モノマーの例を示す図である。

【図6】 測定評価に用いた光学系を示す図である。

【図7】 測定評価の結果を示す図である。

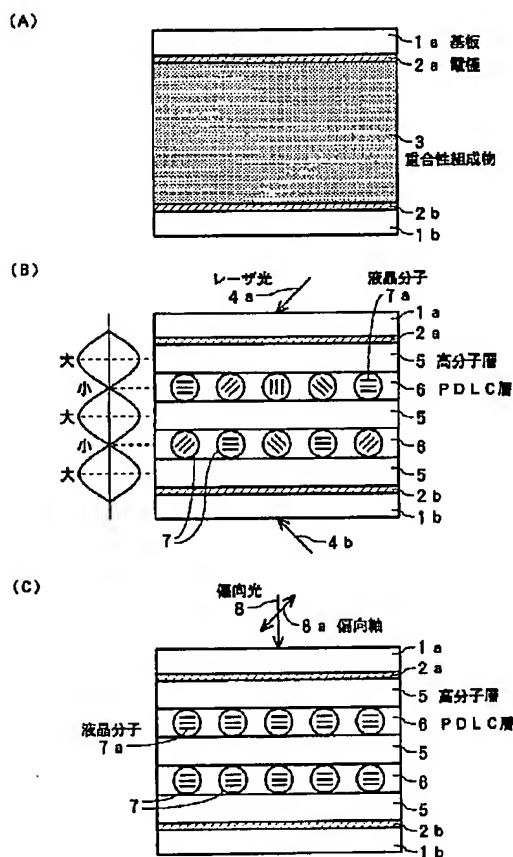
【図8】 従来の高分子分散液晶素子の一例を示す図である。

【図9】 従来の高分子分散液晶素子の他の例を示す図である。

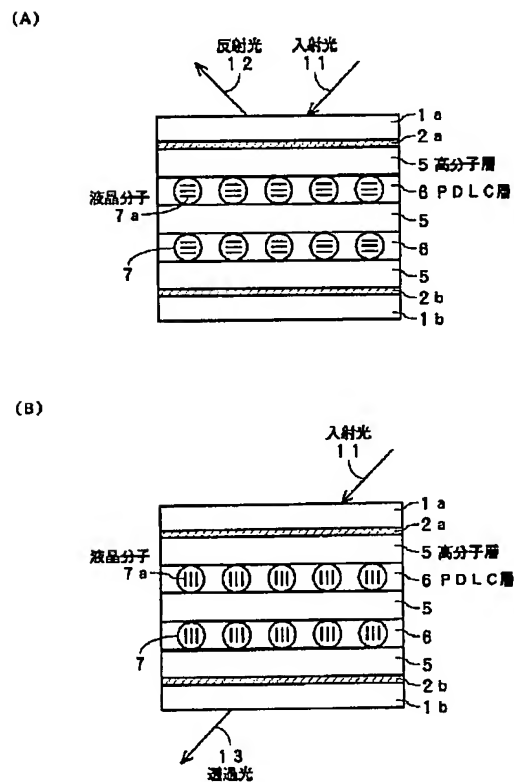
【符号の説明】

- 1 a, 1 b 基板
- 2 a, 2 b 電極
- 3 重合性組成物
- 4 a, 4 b レーザ光
- 5 高分子層
- 6 P D L C層
- 7 液晶領域
- 8 偏向光
- 9 紫外線

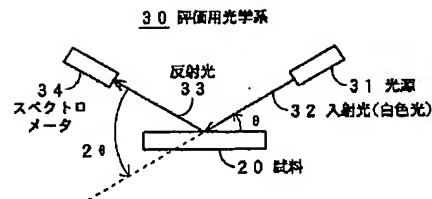
【図1】



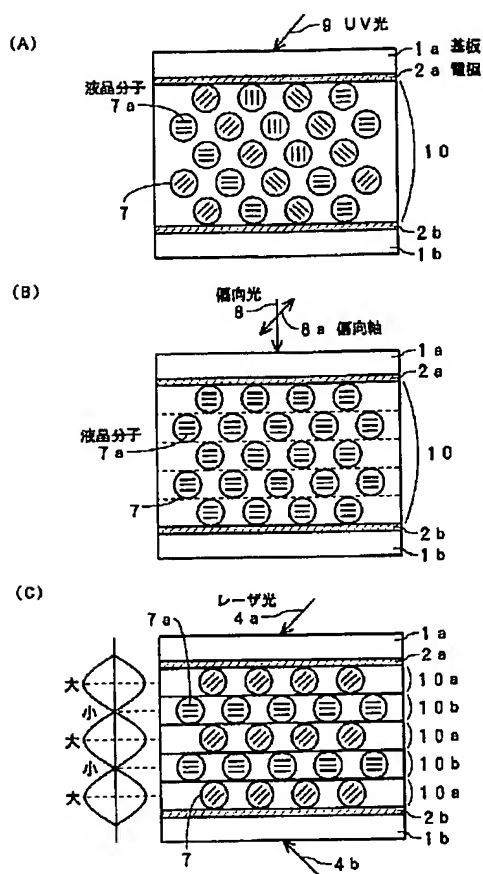
【図2】



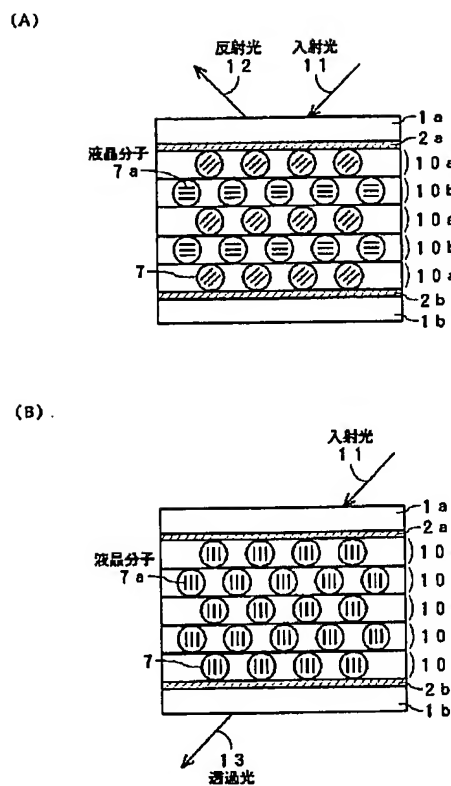
【図6】



【図3】

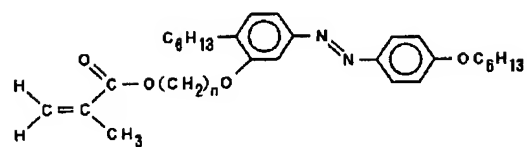


【図4】

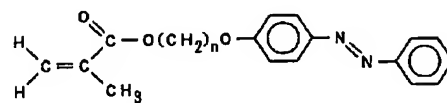


【図5】

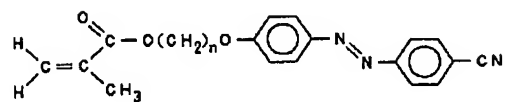
(A)



(B)



(C)

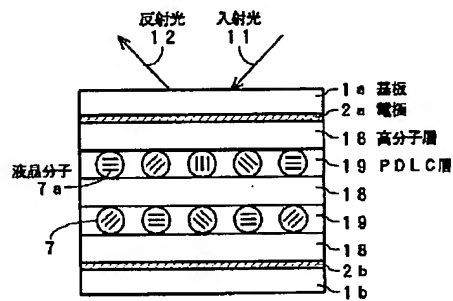


【図 7】

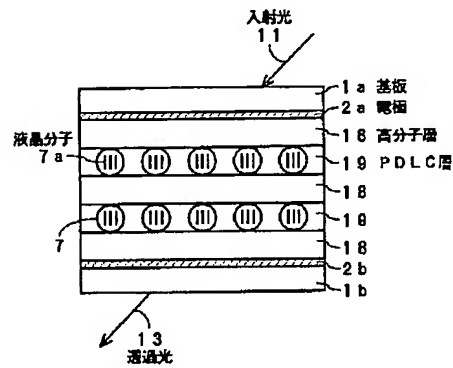
	実施例 1		実施例 2		
	レーザー光 照射前	レーザー光 照射後	偏射前	偏射光 照射後	レーザー光 照射後
反射率[%]	40	50	0	0	80
スペクトル半値幅 [nm]	11	20	-	-	40
評 価	△	○	×	×	☆

【図 9】

(A)

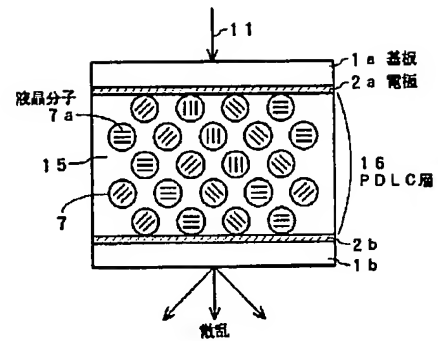


(B)

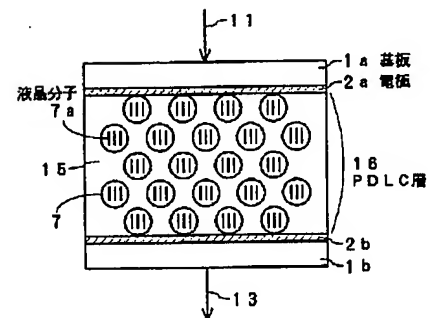


【図 8】

(A)



(B)



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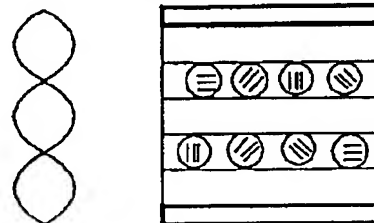
(54) 【発明の名称】 高分子分散型液晶素子及びその製造方法

(57) 【要約】

【課題】 十分な反射率を有し、内部で周期的に屈折率  
 が変化する層構造を有する高分子分散型液晶素子及びそ  
 の製造方法を提供することにある。

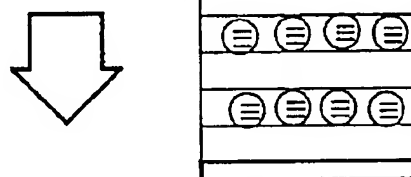
【解決手段】 光2量化性構造を有する重合性化合物と  
 低分子液晶を含有する重合性組成物にレーザー干渉光1  
 1を照射して重合相分離させ、次いで、偏向光12を照  
 射して、低分子液晶が配向した高分子分散型液晶素子を  
 製造する。

レーザー干渉光照射 1 1



(a)

偏向光照射 1 2



(b)

【特許請求の範囲】

【請求項1】 光2量化性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を重合相分離させることにより製造されることを特徴とする高分子分散型液晶素子。

【請求項2】 光2量化性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を重合相分離させ、次いで、偏向光を照射して高分子中の光2量化反応をさせて、低分子液晶を配向させることを特徴とする高分子分散型液晶素子の製造方法。

【請求項3】 光2量化性構造を有する重合性化合物と低分子液晶を含有する重合性組成物に、偏向光を照射して、重合相分離させると同時に光2量化させて、低分子液晶を配向させることを特徴とする高分子分散型液晶素子の製造方法。

【請求項4】 重合相分離をレーザー干渉光の照射により行なうことを特徴とする請求項2記載の高分子分散型液晶素子の製造方法。

【請求項5】 請求項2～4のいずれかに記載の製造方法により製造され、高分子分散型液晶素子内で低分子液晶が配向した構造を有することを特徴とする高分子分散型液晶素子。

【請求項6】 内部で屈折率が周期的に変化する層構造を有することを特徴とする請求項5記載の高分子分散型液晶素子。

【請求項7】 光2量化した高分子化合物と低分子液晶の複合構造で構成され、内部で屈折率が周期的に変化する積層構造を有する高分子分散型液晶素子。

【請求項8】 光2量化性構造を有する重合性化合物と低分子液晶を含有する重合性組成物に、定在波を照射して重合相分離させることを特徴とする請求項7記載の高分子分散型液晶素子の製造方法。

【請求項9】 重合相分離させた後、偏向光を照射して層内の低分子液晶を配向させることを特徴とする請求項8記載の高分子分散型液晶素子の製造方法。

【請求項10】 請求項9記載の製造方法により製造され、層内の低分子液晶が配向したことを特徴とする、光2量化した高分子化合物と低分子液晶の複合構造で構成され、内部で屈折率が周期的に変化する積層構造を有する高分子分散型液晶素子。

【請求項11】 光2量化性構造を有する重合性化合物が、4-アクリロイルアミノフェニルスルホニルアジド、4-メタクロイルアミノフェニルスルホニルアジド、2-p-アジドベンゾイルプロピルアクリレート、2-p-アジドベンゾイルプロピルメタクリレート、シンナミルアクリレート、シンナミルメタクリレート、シンナモイロキシエチルアクリレート、シンナモイロキシエチルメタクリレート、シンナミリデンエチルアクリレート及びシンナミリデンエチルメタクリレートからなる群から選ばれることを特徴とする請求項1、5～7及び10

のいずれかに記載の高分子分散型液晶素子。

【請求項12】 光2量化性構造を有する重合性化合物が、シンナミルアクリレート、シンナミルメタクリレート及びシンナモイロキシエチルメタクリレートであることを特徴とする請求項11記載の高分子分散型液晶素子。

【請求項13】 低分子液晶が、高分子化合物中において、互いに独立して分散することを特徴とする請求項1、5～7及び10～12のいずれかに記載の高分子分散型液晶素子。

【請求項14】 請求項7記載の高分子分散型液晶素子の製造方法であって、(a) 光2量化性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を基板上に塗布する工程、(b) 該重合性組成物を重合相分離させて、高分子分散型液晶層を作製する工程、(c) 該高分子分散型液晶層に偏向光を照射して、低分子液晶を配向させる工程、(d) 低分子液晶が配向した該高分子分散型液晶層上に、光2量化性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を塗布する工程、(e) 該重合性組成物を重合相分離させて、高分子分散型液晶層を作製する工程、及び(f) 該高分子分散型液晶層に、上記(c)で用いた偏向光に対して垂直な振動方向を有する偏向光を照射して、低分子液晶を配向させる工程を含み、上記(a)～(f)の工程を順次繰り返すことを特徴とする製造方法。

【請求項15】 請求項7記載の高分子分散型液晶素子の製造方法であって、(a) 光2量化性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を基板上に塗布する工程、(b) 該重合性組成物に偏向光を照射して、重合相分離させると同時に低分子液晶を配向させ、高分子分散型液晶層を作製する工程、(c) 低分子液晶が配向した該高分子分散型液晶層上に、光2量化性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を塗布する工程、及び(d) 該重合性組成物に偏向光を照射して、重合相分離させると同時に低分子液晶を配向させて高分子分散型液晶を作製する工程を含み、上記(a)～(d)の工程を順次繰り返すことを特徴とする製造方法。

【請求項16】 光2量化性構造を有する重合性化合物が、4-アクリロイルアミノフェニルスルホニルアジド、4-メタクロイルアミノフェニルスルホニルアジド、2-p-アジドベンゾイルプロピルアクリレート、2-p-アジドベンゾイルプロピルメタクリレート、シンナミルアクリレート、シンナミルメタクリレート、シンナモイロキシエチルアクリレート、シンナモイロキシエチルメタクリレート、シンナミリデンエチルアクリレート及びシンナミリデンエチルメタクリレートからなる群から選ばれることを特徴とする請求項2～4、8、9、14及び15のいずれかに記載の高分子分散型液晶素子の製造方法。



【請求項17】 光2量化性構造を有する重合性化合物が、シンナミルアクリレート、シンナミルメタクリレート及びシンナモイロキシエチルメタクリレートであることを特徴とする請求項16記載の高分子分散型液晶素子。

#### 【発明の詳細な説明】

##### 【0001】

【発明の属する技術分野】本発明は、電場や磁場等の印加によって反射率や透過率を制御することが可能な高分子分散型液晶素子およびその製造方法に関するものである。本発明により製造された高分子分散液晶素子は、ディスプレイ、調光素子、光変調素子等の光学素子として応用可能である。

##### 【0002】

【従来の技術】表示用素子および調光素子として、図1に示すような3次元構造のポリマーの空隙中に液晶を分散させた高分子分散型液晶(PDLC)が研究されている。PDLCは、電圧が印加されない状態では、空隙中の液晶の屈折率とポリマーの屈折率の差により界面で入射光が屈折し、膜全体では多数のドロプレットを通過することになり、散乱状態となる(図1a)。また、電圧が印加されると、液晶は基板と垂直に配向し、長軸方向の屈折率とポリマーの屈折率を一致させることにより透明となる(図1b)。このPDLCの技術は偏光板が不要であり、プロジェクタライトバルブへの応用が検討され、明るい表示が期待されている。

【0003】これらの3次元ポリマーの構造は、液晶が分布する空隙が互いに独立に存在したものや、連続的に分布したものがある。このような高分子分散型液晶の製造方法としては、大きく分けて下記の3方法が提案されている。

【0004】第1に、液晶をランダムに配向させることができる多孔質ポリマーに液晶を含浸させる方法。第2に、溶媒中でポリマーと液晶を混合して乳化させた後、溶媒を蒸発させることにより、ポリマーを硬化させる方法。第3に、モノマーやオリゴマーまたはそれらの混合物と液晶を混合した重合性組成物を、熱又は紫外線の照射などの手段を用いて重合させる過程を通して、重合したポリマーと液晶を相分離させる方法。

【0005】また、この高分子分散型液晶の応用として、SPIE.1080,83,(1989)に、内部で周期的に屈折率が変化する高分子分散型液晶素子が開示されている。具体的には図2のように、高分子層と高分子分散型液晶層が交互に積層した構造を作製することにより、屈折率が周期的に変化する層構造を実現したものである。この場合、電圧が印加されない状態では、高分子分散型液晶層と高分子層の周期的な屈折率差に起因した、干渉フィルタの原理による反射光を生じる(図2a)。また、電圧が印加されると、高分子分散型液晶層と高分子層の屈折率が一致して透明となる(図2b)。

##### 【0006】

【発明が解決しようとする課題】図2に示すように、従来の、内部で周期的に屈折率が変化する高分子分散型液晶素子では、高分子分散型液晶層中のドロプレット内の低分子液晶の配向は、高分子分散型液晶層全体ではランダムとなる。従って、高分子分散型液晶層の屈折率は、ドロプレットの一次近似された屈折率( $n_o + 2n_e$ )/3、高分子分散型液晶層中の高分子の屈折率の値( $n_p$ は略 $n_o$ )、高分子分散型液晶層中の低分子液晶の高分子に対する体積分率の値( $v$ )から、 $\{n_o \cdot (3-v) + n_p\} / 3$ という値に低下する。ここで、 $n_p$ はポリマーの屈折率、 $n_o$ は光の電場の振動方向が液晶分子の長軸と直交する場合の屈折率、 $n_e$ は光の電場の振動方向が液晶分子の長軸と平行な場合の屈折率を示す。このため、高分子分散型液晶層と高分子層との屈折率差が小さくなり、高い反射率が得られないという問題があった。よって、内部で周期的に屈折率が変化する高分子分散型液晶素子の反射率を高めるために、素子中の低分子液晶の配向を揃える技術が求められているが、そのような技術は未だ知られていない。

【0007】類似の技術として、PDLC中の初期状態におけるドロプレット内の低分子液晶の配向方向を制御する技術はいくつか提案されている。例えば、①USP5,188,760には、液晶性高分子を用いたPDLCと配向膜との組合せによる配向制御技術が開示されている。この技術では、液晶性モノマーをPDLCの前駆体である重合性組成物に用い、それを配向膜付きセルに注入する。この状態でUVや熱を加えることにより、液晶性モノマーの重合体である液晶性高分子と低分子液晶が配向膜の方向に配向した状態で重合相分離を行ない、液晶性モノマー硬化後には、低分子液晶の配向が固定される。

【0008】また、②特開平5-281527には、PDLCと水平外部磁場や電場との組合せによる配向制御技術が開示されている。この技術では、重合性組成物を配向膜のないセルの内部に注入し、このセルに対して水平方向に外部磁場や電場を印加した状態でUVや熱を加えることにより、低分子液晶が外部磁場や電場の方向に配向した状態で重合相分離を行ない、重合性組成物硬化後に、低分子液晶の配向が固定される。

【0009】また、③Japan Display '92, 699には、PDLCと配向膜との組合せによる配向制御技術が開示されている。この技術では、PDLCの前駆体である重合性組成物を、液晶濃度が非常に高い液晶相となるように調製し、それを配向膜付きセルに注入する。この状態では、液晶相状態の重合性組成物は配向膜の方向に配向しているが、この状態にUVや熱を加えて、配向膜付きセルの内部で重合相分離させることにより、初期配向の状態を保ったまま低分子液晶の配向が固定される。

【0010】さらに、④Mol.Mat., 2,295 (1993)に

は、光2量性構造を有する高分子化合物を用いた配向制御技術が開示されている。この技術は、材料として光2量性構造を有する高分子化合物を用いた含浸法で作製するものである。まず、乳化法で、光2量性構造を有する高分子化合物と該高分子化合物の貧溶媒からなる複合膜を作製し、この複合膜から貧溶媒を抽出し、乾燥させて、光2量性構造を有する高分子化合物からなる多孔質ポリマーを作製する。さらに、この多孔質ポリマーに低分子液晶を含浸させて、光2量性構造を有する高分子化合物からなるPDL Cを作製する。このPDL Cに偏向光を照射して光2量化反応を起こさせる。この光2量化反応による高分子化合物の構造変化に伴い、低分子液晶は配向する。

【0011】しかしながら、このうち、①及び③の配向固定方法では、配向膜を用いなければならないために、図2のような複合構造を作製することができなかった。また、②の配向固定方法では、セルと平行に外部磁場や電場を印加しなければならないが、セルサイズが大きい場合は、セルの面内一面にわたって有効な外部磁場や電場を印加することが非常に困難であった。例えば、特開平5-281527には、外部電場を印加する場合は、外部電場の大きさが1kV/cm以上であることが必要であるとの記載がある。ここで、セルサイズが対角12インチであると仮定すると、印加電圧は約350kV以上必要となる計算になるが、このように大きな印加電圧は容易には実現できない。さらに、④は、材料として光2量性構造を有する高分子化合物を用いるため、含浸法でしか作製できない。また、④で得られる膜は、液晶を浸透させるために、全ての空隙が膜表面と繋がっている必要がある。独立した空隙は水の残存または、気泡となり、特性の信頼性に影響を与えるので、望ましくない。また、膜が柔軟性を有するために、水の除去と液晶の含浸工程において膜が変形しやすく、対抗基板を張り合わせる際に、膜厚を制御するのが困難である。さらに、④の方法では、図3に示す周期構造のような複合構造を作製することが不可能である。このように、従来の液晶配向方法はいずれも問題点を有しており、十分な反射率を有し、内部で周期的に屈折率が変化する高分子分散型液晶素子は未だ得られていない。

#### 【0012】

【課題を解決するための手段】本発明者らは、上記の従来技術の課題を解決する手段として、下記の手段を見出し、本発明を完成させた。即ち、本発明は、光2量性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を重合相分離させることにより製造されることを特徴とする高分子分散型液晶素子である。本発明はまた、光2量性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を重合相分離させ、次いで、偏向光を照射して高分子中の光2量化反応をさせて、低分子液晶を配向させることを特徴とする高分子分散型液晶

素子の製造方法である。

【0013】本発明はまた、光2量性構造を有する重合性化合物と低分子液晶を含有する重合性組成物に、偏向光を照射して、重合相分離させると同時に光2量化させて、低分子液晶を配向させることを特徴とする高分子分散型液晶素子の製造方法である。本発明はまた、前記製造方法により製造され、高分子分散型液晶素子内で低分子液晶が配向した構造を有し、内部で屈折率が周期的に変化する層構造を有することを特徴とする高分子分散型液晶素子である。本発明はまた、光2量化した高分子化合物と低分子液晶の複合構造で構成され、内部で屈折率が周期的に変化する積層構造を有する高分子分散型液晶素子である。

【0014】本発明はまた、(a) 光2量性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を基板上に塗布する工程、(b) 該重合性組成物を重合相分離させて、高分子分散型液晶層を作製する工程、

(c) 該高分子分散型液晶層に偏向光を照射して、低分子液晶を配向させる工程、(d) 低分子液晶が配向した該高分子分散型液晶層上に、光2量性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を塗布する工程、(e) 該重合性組成物を重合相分離させて、高分子分散型液晶層を作製する工程、及び(f) 該高分子分散型液晶層に、上記(c) で用いた偏向光に対して垂直な振動方向を有する偏向光を照射して、低分子液晶を配向させる工程を含み、上記(a) ~ (f) の工程を順次繰り返すことを特徴とする、前記の内部で屈折率が周期的に変化する積層構造を有する高分子分散型液晶素子の製造方法である。

【0015】本発明はまた、(a) 光2量性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を基板上に塗布する工程、(b) 該重合性組成物に偏向光を照射して、重合相分離させると同時に低分子液晶を配向させ、高分子分散型液晶層を作製する工程、(c) 低分子液晶が配向した該高分子分散型液晶層上に、光2量性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を塗布する工程、及び(d) 該重合性組成物に偏向光を照射して、重合相分離させると同時に低分子液晶を配向させて高分子分散型液晶を作製する工程を含み、上記(a) ~ (d) の工程を順次繰り返すことを特徴とする、前記の内部で屈折率が周期的に変化する積層構造を有する高分子分散型液晶素子の製造方法である。以下、本発明について詳しく説明する。

#### 【0016】

【発明の実施の形態】最初に、本発明の高分子分散型液晶素子の製造方法を、好適具体例に基づいて説明する。本発明の高分子分散型液晶素子は、光2量性構造を有する重合性化合物、低分子液晶及び重合性基の重合開始剤を混合して重合性組成物を調液し、セルに注入する。このセルに、レーザー干渉光を照射すると、レーザー干

渉光の振幅の大きな領域では重合性化合物の硬化が起こり、屈折率の低い高分子層が形成される。また、レーザー干渉光の振幅の小さな領域では重合相分離が起こり、屈折率の高い高分子分散型液晶層が形成される。レーザー干渉光の振幅の大きな領域と小さな領域は、空間的に交互に繰り返すため、周期的に屈折率が変化する層構造を有する高分子分散型液晶素子が作製される（図4a）。

【0017】この高分子分散型液晶素子中の低分子液晶の配向は、上記のようにして製造した高分子分散型液晶素子（図4a）に、一様に偏向した光を照射することによって達成される（図4b）。偏向した光の波長は、光2量化性構造を有する高分子化合物の種類によって異なるが、例えば、シンナメート系化合物の場合は、250nm～350nmの光を用いることができる。偏向光の照射時間は、光の強度や、光2量化性構造の感度、照射雰囲気によっても異なるが、1分～120分程度の照射とすることが好ましい。

【0018】また、光2量化性構造を有する高分子化合物と重合性化合物の重合開始剤とが同時に感度を有する波長の偏向光を用いる場合は、重合相分離と低分子液晶の配向制御を同時に行うことができる。

【0019】次に、本発明の「内部で周期的に屈折率が変化する積層構造を有する高分子分散型液晶素子」の製造方法について説明する。本製造方法は、重合相分離と光2量化を用いた塗布積層方法によるものであるが、重合相分離と光2量化を順次起こさせ、それを繰り返す方法（図5）と、重合相分離と光2量化を同時に起こさせ、それを繰り返す方法（図6）がある。

【0020】最初に、重合相分離と光2量化を順次起こさせ、それを繰り返す方法について説明する。本方法は、図5に示すように、（a）光2量化性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を基板上に塗布する工程、（b）該重合性組成物に光や熱を加えて、重合相分離させて光2量化性構造を有する高分子化合物中に低分子液晶が分散した高分子分散型液晶層を作製する工程、（c）該高分子分散型液晶層に偏向光を照射して、光2量化性構造を有する高分子化合物に光2量化を起こさせ、高分子分散型液晶層中の低分子液晶を配向させる工程、（d）低分子液晶が配向した該高分子分散型液晶層上に、光2量化性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を基板上に塗布する工程、（e）該重合性組成物に光や熱を加えて、重合相分離させて高分子分散型液晶層を作製する工程、（f）該高分子分散型液晶層に、（c）で用いた偏向光とは垂直な振動方向を有する偏向光を照射して、光2量化性構造を有する高分子化合物に光2量化を起こさせ、低分子液晶を配向させる工程からなり、この（a）～（f）の工程を順次繰り返すことにより、図5（g）に示すような「内部で周期的に屈折率が変化する層構造を

有する高分子分散型液晶素子」を製造することができる。尚、規則正しい層構造を得るために、定在波を照射することにより重合相分離を起こさせることが好ましい。

【0021】次に、重合相分離と光2量化を同時に起こさせ、それを繰り返す方法について説明する。本方法は、図6に示すように、（a）光2量化性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を基板上に塗布する工程、（b）該重合性組成物に偏向光を照射して、重合相分離と光2量化性構造を有する重合性化合物の光2量化を同時に起こさせ、低分子液晶が配向した高分子分散型液晶を作製する工程、（c）低分子液晶が配向した該高分子分散型液晶層上に、光2量化性構造を有する重合性化合物と低分子液晶を含有する重合性組成物を基板上に塗布する工程、（d）該重合性組成物に、（b）で用いた偏向光とは垂直な振動方向を有する偏向光を照射して、重合相分離と重合性化合物の光2量化を同時に起こさせ、低分子液晶が配向した高分子分散型液晶を作製する工程からなり、（a）～（d）の工程を順次繰り返すことにより、図6（e）のような「内部で周期的に屈折率が変化する積層構造を有する高分子分散型液晶素子」を製造することができる。尚、本方法においても、規則正しい層構造を得るために、定在波を照射することにより重合相分離を起こさせることが好ましい。

【0022】本発明において用いられる重合性組成物は、光2量化性構造を有する重合性化合物、低分子液晶化合物及び重合開始剤を含有する。本発明の「光2量化性構造を有する重合性化合物」は、光2量化性構造を有する化合物に、重合性基であるアクリロイル基やメタクロイル基を付与した化合物またはその誘導体であれば、特に限定されない。このような化合物またはその誘導体の例としては、4-アクリロイルアミノフェニルスルホンアジド、4-メタクロイルアミノフェニルスルホンアジド、2-p-アジドベンゾイルプロピルアクリレート、2-p-アジドベンゾイルプロピルメタクリレート、シンナミルアクリレート、シンナミルメタクリレート、シンナモイロキシエチルアクリレート、シンナモイロキシエチルメタクリレート、シンナミリデンエチルアクリレート、シンナミリデンエチルメタクリレート等を挙げることができる。これらの中でも、シンナミルアクリレート、シンナミルメタクリレート及びシンナモイロキシエチルメタクリレートは好適に用いることができる。これらの「光2量化性構造を有する重合性化合物」は、単独で用いても、複数を組み合わせて用いてもよい。また、「光2量化性構造を有する重合性化合物」は、それだけでも感光性を有するが、感光感度を増加させたり、感光波長を選択するためには、感光色素や増感剤等と併用することが好ましい。

【0023】また、高分子組成物中に含まれる低分子液

晶を構成する液晶化合物としては、ネマチック液晶、コレステリック液晶、スメクチック液晶及び強誘電性液晶等や、一般的に電界駆動型表示材料として使用されている種々の低分子液晶化合物を使用することができる。このような低分子液晶化合物の具体的な例としては、ビフェニル系、フェニルベンゾエート系、シクロヘキシルベンゼン系、アゾキシベンゼン系、アゾベンゼン系、ターフェニル系、ビフェニルベンゾエート系、シクロヘキシルビフェニル系、フェニルピリミジン系、シクロヘキシルピリミジン系等の各種低分子液晶化合物を挙げることができる。これらの低分子液晶化合物は、一般に使用されている低分子液晶材料と同様に、単独で用いても、複数を組み合わせて用いてもよい。

【0024】また、本発明において使用される重合性組成物は、前記の「光2量化性構造を有する重合性化合物」を必須の構成成分として含有するものであるが、それ以外の種々の重合性化合物を含有することができる。このような重合性化合物の例としては、例えば、アクリル酸アルキルエステル、アクリルアミド、アクリル酸ヒドロキシエステル、メタクリル酸アルキルエステル、メタクリルアミド、メタクリル酸ヒドロキシエステル、ビニルピロリドン、スチレン及びその誘導体、アクリロニトリル、塩化ビニル、塩化ビニリデン、エチレン、ブタジエン、イソブレン、ビニルピリジン等の単官能および多官能モノマーを挙げることができる。

【0025】さらに、本発明の重合性組成物は、重合性化合物を重合させるための重合開始剤を含有する。重合開始剤は、内部で周期的に屈折率が変化する高分子分散型液晶素子を製造する際に用いる定在波の波長に感度を有する材料の中から選択することができる。本発明においては、例えば、N-フェニルグリシン、アゾイソブチロニトリル等を好適に用いることができる。

【0026】尚、本発明の高分子分散型液晶素子のデバイス形態としては、通常の液晶表示素子と同様に、2つの電極板からなるセルに挟まれた構造が好ましい。電極板としては、例えば、表面にITOを施したガラス基板やプラスチックフィルム、NESAガラス基板等の透明電極付基板を好適に用いることができる。

【0027】

【作用】本発明の光2量化性構造を有する高分子化合物と低分子液晶の複合構造で構成され、内部で屈折率が周期的に変化する層構造を有する高分子分散型液晶素子において、光2量化性構造を有する高分子化合物に偏向光が照射されると、光2量化性構造を有する高分子化合物の光吸収係数の異方性から、偏向光の振動方向と平行な方向に強い吸収を有する光2量化性構造が効率的に反応し、該高分子分散型液晶素子中の高分子が光2量化する。そして、この光2量化は分子の構造変化を伴うが、特定の方向を向いた分子の構造変化に伴い、低分子液晶は特定の方向へ配向するようになる(図3)。その結果、従

来の高分子分散型液晶素子よりも光反射率の高い、内部で屈折率が周期的に変化する層構造を有する高分子分散型液晶素子の製造が可能となる。

【0028】

【実施例】以下、実施例により本発明をさらに詳しく説明する。

実施例1

2量化性構造を有する重合性化合物として、シンナモイロキシエチルメタクリレートを合成した。合成したシンナモイロキシエチルメタクリレート0.08g、重合性化合物としてジペンタエリスルトールヘキサアクリレート(日本化薬社製)0.67g、重合性化合物の重合開始剤としてローズベンガル(日本化薬社製)3.5mgとN-フェニルグリシン(和光純薬社製)0.01g及び低分子液晶E7(メルク社製)0.2gを混合して、重合性組成物を調液した。次に、この重合性組成物を、透明電極(ITO)付き石英基板を対抗に張り合わせたセル(10 $\mu$ m)内に注入した。488nmのArイオン・レーザー光を2光束に分け、それぞれセルの裏表からセル表面に照射した。これら2光束はセル内で干渉光を形成した。このレーザー光を10分間照射した後、高圧水銀灯を光源とした偏向紫外線を60分間照射して、内部で屈折率が周期的に変化する層構造を有する高分子分散型液晶素子を製造した。

【0029】実施例2

2量化性構造を有する重合性化合物としてシンナミルメタクリレート(ポリサイエンス社製)0.05g、重合性化合物としてヘキサジオールジアクリレート(日本化薬社製)0.05g、重合性化合物の重合開始剤としてアゾイソブチロニトリル(和光純薬社製)1.5mg及び低分子液晶E7(メルク社製)0.5gを混合し、重合性組成物を調液した。この重合性組成物を、透明電極(ITO)付き石英基板上に塗布し、高圧水銀灯を光源とした偏向紫外線を60分間照射し、重合相分離と光2量化を同時に行い、高分子分散型液晶層を製造した。

【0030】実施例3

2量化性構造を有する重合性化合物としてシンナミルメタクリレート(ポリサイエンス社製)0.05g、重合性化合物としてヘキサジオールジアクリレート(日本化薬社製)0.05g、重合性化合物の重合開始剤としてアゾイソブチロニトリル(和光純薬社製)1.5mg及び低分子液晶E7(メルク社製)0.5gを混合し、重合性組成物を調液した。この重合性組成物を、透明電極(ITO)付き石英基板上に塗布し、70℃のオープンの中で24時間反応させて高分子分散型液晶層を作製した。この高分子分散型液晶層に、高圧水銀灯を光源とした偏向紫外線を60分間照射し、光2量化を行った。次に、この高分子分散型液晶層上に、前記重合性組成物を再び塗布し、70℃のオープンの中で24時間反応させて、高分子分散型液晶層を積層した。さらに、この高

子分散型液晶層に、前回とは振動方向が垂直な偏向紫外線を60分間照射し、光2量化を行った。これらの工程を繰り返して、厚さ10 $\mu\text{m}$ の内部で屈折率が周期的に変化する積層構造を有する高分子分散型液晶素子を製造した。

#### 【0031】実施例4

2量化性構造を有する重合性化合物としてシンナミルメタクリレート（ポリサイエンス社製）0.05g、重合性化合物としてヘキサジオールジアクリレート（日本化薬社製）0.05g、重合性化合物の重合開始剤としてアゾイソブチロニトリル（和光純薬社製）1.5mg及び低分子液晶E7（メルク社製）0.5gを混合し、重合性組成物を調液した。この重合性組成物を、透明電極（ITO）付き石英基板上に塗布し、高圧水銀灯を光源とした偏向紫外線を60分間照射し、重合相分離と光2量化を同時に行い、高分子分散型液晶層を作製した。次に、この高分子分散型液晶層上に、前記重合性組成物を再び塗布し、前回とは振動方向が垂直な偏向紫外線を高分子分散型液晶層に60分間照射し、重合相分離と光2量化を同時に行い、高分子分散型液晶層を積層した。これらの工程を繰り返して、厚さ10 $\mu\text{m}$ の内部で屈折率が周期的に変化する積層構造を有する高分子分散型液晶素子を製造した。

【0032】ここで、上記実施例1～4について簡単にまとめると、実施例1は、レーザー干渉光を用いて重合相分離を行った後、光2量化を行い、内部で屈折率が周期的に変化する層構造を有する高分子分散型液晶素子を製造した例である。実施例2は、重合相分離と光2量化を同時に行い、高分子分散型液晶層を製造した例である。実施例3は、重合相分離と光2量化を順次行う方法により、内部で屈折率が周期的に変化する積層構造を有する高分子分散型液晶素子を製造した例である。さらに、実施例4は、重合相分離と光2量化を同時に行う方法によ

り、内部で屈折率が周期的に変化する積層構造を有する高分子分散型液晶素子を製造した例である。

#### 【0033】比較例1

シンナモイロキシエチルメタクリレートを用いないこと以外は、実施例1と同様にして、内部で屈折率が周期的に変化する層構造を有する高分子分散型液晶素子を製造した。

#### 【0034】比較例2

無偏向紫外線を用いたこと以外は、実施例2と同様にして、高分子分散型液晶素子層を製造した。

#### 【0035】比較例3

シンナミルメタクリレートを用いないこと以外は、実施例3と同様にして、内部で屈折率が周期的に変化する積層構造を有する高分子分散型液晶素子を製造した。

#### 【0036】比較例4

シンナミルメタクリレートを用いないこと以外は、実施例4と同様にして、内部で屈折率が周期的に変化する積層構造を有する高分子分散型液晶素子を製造した。

#### 【0037】試験例1（反射率の評価）

実施例1、3、4及び比較例1、3、4において製造した各高分子分散型液晶素子を評価試料とし、反射率を以下の方法により評価した。

（反射率評価方法）評価試料の反射率を、図7に示すゴニオメーターヘッドを用いた $\Theta$ -2 $\Theta$ 光学系、白色光源及びスペクトロメーターを組み合わせた評価装置により評価した。

（反射率の評価結果）高分子分散型液晶素子の反射率評価の目安として、反射率30%以下を×、30%～50%を△、50%～70%を○、70%以上を◎とした。結果を表1に示す。結果を表1に示す。

#### 【0038】

【表1】

表1 反射率の評価結果

	実施例1	実施例3	実施例4	比較例1	比較例3	比較例4
反射率(%)	72	78	88	48	42	40
評価	◎	◎	◎	△	△	△

【0039】表1から明らかであるように、実施例1、3、4の評価試料は、比較例1、3、4の評価試料と比べて、反射率が著しく高い。

#### 【0040】試験例2（配向特性の評価）

実施例2及び比較例2において製造した各高分子分散型液晶素子を評価試料とし、配向特性を以下の方法により評価した。

（配向特性評価方法）偏光顕微鏡において、ポラライザーとアナライザーを平行（クロスニコル状態）に設置

し、評価試料に対して白色光（入射光）を垂直に照射した。評価試料を入射光に対して垂直な面内で回転させ、試料からの透過光強度をフォトダイオードで検出し、透過光強度の角度依存性を調べた。

（配向特性の評価結果）配向特性の評価結果を図8に示す。図8の（A）と（B）は、それぞれ実施例2と比較例2の結果である。図8（A）では、液晶が配向して高分子分散型液晶素子が光学的異方性を有しているのに対し、図8（B）では、光学的異方性がないことが解る。

この結果から、本発明の高分子分散型液晶素子は、素子中の低分子液晶が配向し、素子として光学的に異方性を有することが明らかとなった。

【0041】

【発明の効果】本発明によれば、内部で屈折率が周期的に変化する層構造を有する高分子分散型液晶素子中の低分子液晶の配向制御が可能となる。また、本発明の方法によれば、従来の高分子分散型液晶素子に比べて、光反射率が高く、内部で屈折率が周期的に変化する層構造を有する高分子分散型液晶素子が得られる。

【図面の簡単な説明】

【図1】従来の高分子分散型液晶の模式図である。

(a)は電圧非印加の状態を、(b)は電圧印加の状態を示す。

【図2】従来の、内部で屈折率が周期的に変化する層構造を有する高分子分散型液晶素子の模式図である。

(a)は電圧非印加の状態を、(b)は電圧印加の状態を示す。

【図3】本発明の高分子分散型液晶素子の模式図である。(a)は電圧非印加の状態を、(b)は電圧印加の状態を示す。

【図4】本発明の、内部で屈折率が周期的に変化する層構造を有する高分子分散型液晶素子の製造方法の1つを示す図である。(a)はレーザー干渉光照射工程を、(b)は偏向光照射工程を示す。

【図5】本発明の、内部で屈折率が周期的に変化する層構造を有する高分子分散型液晶素子の製造方法の1つを示す図である。(a)～(f)は各工程を示し、

(g)は本製造方法により得られる本発明の高分子分散型液晶素子の構造を示す。

【図6】本発明の、内部で屈折率が周期的に変化する層構造を有する高分子分散型液晶素子の製造方法の1つを示す図である。(a)～(d)は各工程を示し、

(e)は本製造方法により得られる本発明の高分子分散型液晶素子の構造を示す。

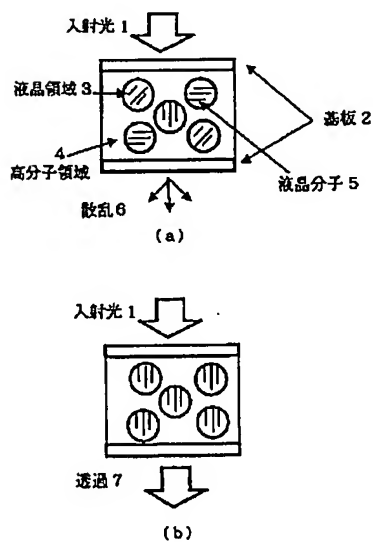
【図7】反射率評価に用いた光学系の配置を示す図である。

【図8】高分子分散型液晶素子の透過光強度の角度依存性を示すグラフである。(A)は実施例2の結果を、(B)は比較例2の結果を示す。

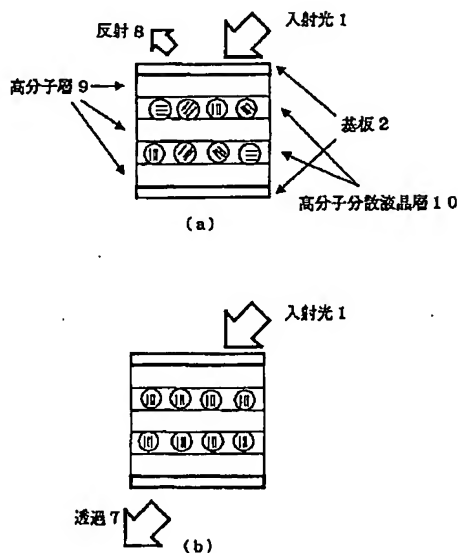
【符号の説明】

- 1 入射光
- 2 基板
- 3 液晶領域
- 4 高分子領域
- 5 液晶分子
- 6 散乱
- 7 透過
- 8 反射
- 9 高分子層
- 10 高分子分散液晶層
- 11 レーザー干渉光照射
- 12 偏向光照射
- 13 スペクトロメーター
- 14 白色光源
- 15 評価試料

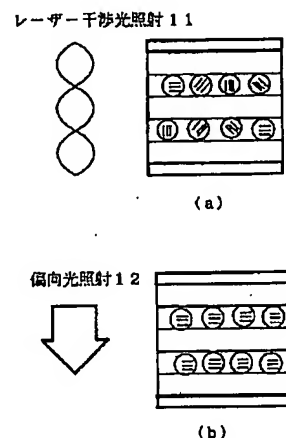
【図1】



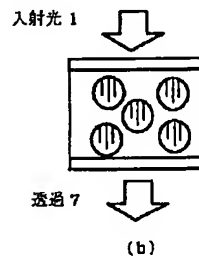
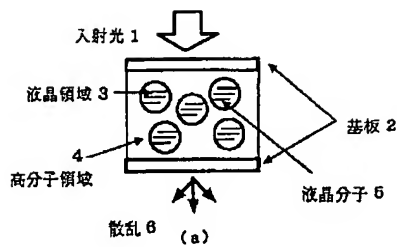
【図2】



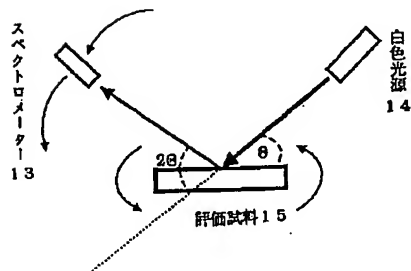
【図4】



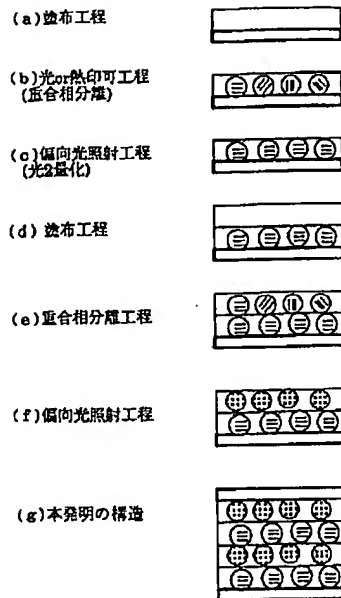
【図3】



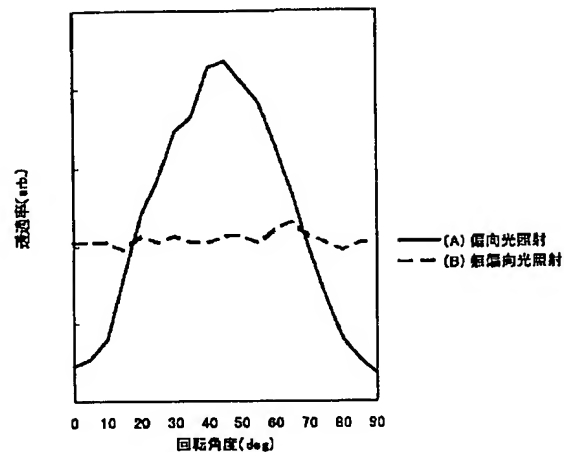
【図7】



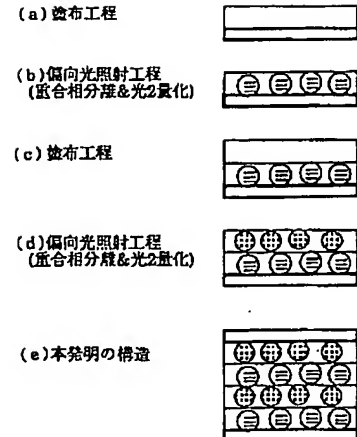
【図5】



【図8】



【図6】



フロントページの続き

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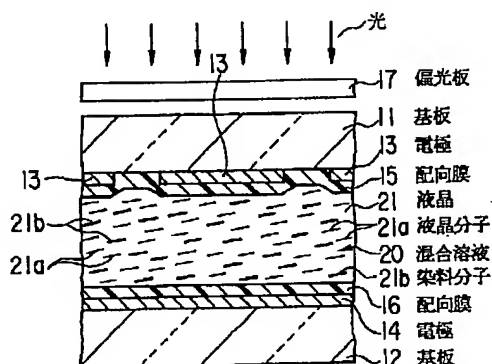
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(54) 【発明の名称】 高分子分散型液晶素子の製造方法

(57) 【要約】

【目的】 混合溶液への照射光を効率よく高分子材料の光重合に利用して、混合溶液への照射光量を多くすることなく良好な光散乱性をもつ液晶／高分子複合膜を形成する。

【構成】 基板11、12間に、光により重合反応する高分子材料と二色性染料を含む液晶との混合溶液20の層を設け、その二色性染料の分子21bを所定方向にほぼ一様に配向させた状態で、前記混合溶液20に偏光板17を介して、二色性染料の分子長軸方向の吸収軸に対して直交する方向と偏光板17を透過した直線偏光の偏光方向とのなす角 $\phi$ と偏光板17の透過率 $x$ とが、 $x \geq (\pi/2) \sin \phi$ と $x \geq [\pi / (\pi + 2)] (\sin \phi + \cos \phi)$ とを満たす条件で光を照射し、前記高分子材料を光重合させて液晶／高分子複合膜を形成する。





【特許請求の範囲】

【請求項1】 一对の基板間に、高分子層中に二色性染料を含む液晶を分散させてなる液晶／高分子複合膜を設けた高分子分散型液晶素子の製造方法であって、  
一对の基板間もしくは一方の基板上に、光により重合反応する高分子材料と二色性染料を含む液晶との混合溶液の層を設け、その二色性染料の分子を所定方向にほぼ一様に配向させた状態で、前記混合溶液に、偏光板を介して、

前記二色性染料の分子長軸方向の吸収軸に対して直交する方向と前記偏光板を透過した直線偏光の偏光方向とのなす角 $\phi$ と、前記偏光板の透過率 $\chi$ とが、

$$\chi > (\pi/2) \sin \phi$$

を満たし、

かつ、前記二色性染料の二色性比 $\kappa$ が、

$$\kappa > (\chi - \cos \phi) / (\sin \phi - 2\chi/\pi)$$

である条件で光を照射し、前記高分子材料を光重合させて液晶／高分子複合膜を形成することを特徴とする高分子分散型液晶素子の製造方法。

【請求項2】 一对の基板間に、高分子層中に二色性染料を含む液晶を分散させてなる液晶／高分子複合膜を設けた高分子分散型液晶素子の製造方法であって、  
一对の基板間もしくは一方の基板上に、光により重合反応する高分子材料と二色性染料を含む液晶との混合溶液の層を設け、その二色性染料の分子を所定方向にほぼ一様に配向させた状態で、前記混合溶液に、偏光板を介して、

前記二色性染料の分子長軸方向の吸収軸に対して直交する方向と前記偏光板を透過した直線偏光の偏光方向とのなす角 $\phi$ と、前記偏光板の透過率 $\chi$ とが、

$$\chi > [\pi / (\pi + 2)] (\sin \phi + \cos \phi)$$

を満たし、

かつ、前記二色性染料の二色性比 $\kappa$ が、

$$\kappa < (\chi - \cos \phi) / (\sin \phi - 2\chi/\pi)$$

である条件で光を照射し、前記高分子材料を光重合させて液晶／高分子複合膜を形成することを特徴とする高分子分散型液晶素子の製造方法。

【請求項3】 一对の基板間に、高分子層中に二色性染料を含む液晶を分散させてなる液晶／高分子複合膜を設けた高分子分散型液晶素子の製造方法であって、  
一对の基板間もしくは一方の基板上に、光により重合反応する高分子材料と二色性染料を含む液晶との混合溶液の層を設け、その二色性染料の分子を所定方向にほぼ一様に配向させた状態で、前記混合溶液に、偏光板を介して、

前記二色性染料の分子長軸方向の吸収軸に対して直交する方向と前記偏光板を透過した直線偏光の偏光方向とのなす角 $\phi$ と、前記偏光板の透過率 $\chi$ とが、

$$\chi \geq (\pi/2) \sin \phi$$

$$\chi \geq [\pi / (\pi + 2)] (\sin \phi + \cos \phi)$$

を満たす条件で光を照射し、前記高分子材料を光重合させて液晶／高分子複合膜を形成することを特徴とする高分子分散型液晶素子の製造方法。

【請求項4】 混合溶液に照射する光は、所定方向にほぼ一様に配向された二色性染料の分子長軸方向の吸収軸に対してほぼ垂直な方向から入射させることを特徴とする請求項1～3のいずれか1つに記載の高分子分散型液晶素子の製造方法。

【請求項5】 二色性染料は、正の二色性を有するp型染料であることを特徴とする請求項1～3のいずれか1つに記載の高分子分散型液晶素子の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 この発明は、高分子分散型液晶素子の製造方法に関するものである。

【0002】

【従来の技術】 最近、液晶素子として、一般に用いられているTN型やSTN型の液晶素子に比べて非常に明るい表示が得られる高分子分散型液晶素子が注目されている。図10は従来の高分子分散型液晶素子の断面図、図11はその一部分の拡大図であり、この高分子分散型液晶素子は、表示用の透明電極3、4を設けた一对の透明基板1、2を枠状のシール材5を介して接合し、この両基板1、2間に、液晶／高分子複合膜6を設けた構成となっている。

【0003】 上記液晶／高分子複合膜6は、図11に示すように、透明な高分子層7中に液晶8を分散を分散させたもので、前記液晶8としては一般に、誘電異方性が正のネマティック液晶が用いられており、さらに、この液晶8には二色性染料が添加されている。図11において、8aは液晶の分子を示し、8bは前記二色性染料の分子を示している。

【0004】 この高分子分散型液晶素子は、上記液晶／高分子複合膜6での光の散乱と透過とを利用して表示するものであり、この複合膜6の高分子層7中に分散している液晶8の液晶分子8aは、電界が印加されていない状態では図11のようにランダムな方向を向いており、同様に染料分子8bもランダムな方向を向いているため、この無電界状態では、液晶素子に入射した光が、前記複合膜6を通る際に、高分子層7と液晶8との界面および液晶8の光散乱作用により散乱されるとともに、その散乱光のうちの二色性染料の吸収波長域の光が前記二色性染料によって吸収され、表示が二色性染料の色に着色された着色表示となる。

【0005】 また、両基板1、2の電極3、4間に電圧を印加すると、その電界によって液晶分子8aが立上り配向し、それに連れて染料分子8bも立上り配向するため、この電界印加状態では、液晶素子に入射した光が、複合膜6での光散乱作用をほとんど受けることなく、また二色性染料による吸収もほとんど受けることなく複合

膜6を透過し、表示がほぼ無彩色の明表示となる。

【0006】このため、上記高分子分散型液晶素子は、TN型やSTN型の液晶素子に必要な不可欠な偏光板が不要であり、したがって偏光板での光吸収による光量ロスが無いから、非常に明るい表示が得られる。

【0007】なお、上記高分子分散型液晶素子は、一般に、その裏面に反射板（図示せず）を配置して反射型素子として使用されており、この反射型素子においては、その表面側から入射した光が液晶／高分子複合膜6を通過して反射板で反射され、再び前記複合膜6を通過して表面側に出射するため、無電界部を通る光が二重に散乱されるとともに二色性染料で吸収されて、着色表示がより鮮明になる。

【0008】上記高分子分散型液晶素子は、一般に、一対の基板1，2をシール材5を介して接合した後、この両基板1，2間に、光によって重合反応する高分子材料と二色性染料を含む液晶との混合溶液を真空注入法により充填して混合溶液の層を設け、この混合溶液に、いずれか一方の基板の外側から光（紫外線）を照射して、前記高分子材料を光重合させる方法で製造されている。

【0009】このように、基板1，2間の混合溶液に光を照射すると、モノマーあるいはオリゴマーの状態にある高分子材料が、その二重結合が解けることによってラジカル化し、隣り合う分子のラジカルが互いに結合し合うラジカル重合反応により高分子となって、この高分子材料のポリマー化により、液晶が二色性染料とともに相分離する。

【0010】このため、ポリマー化した高分子の層7は、図11のようなスポンジのような断面をもち、この高分子層7の各隙間部に、二色性染料を含む液晶8が閉じ込められて、上述した構造の液晶／高分子複合膜6が形成される。なお、この複合膜の形成方法は、一般に光重合相分離法と呼ばれている。

【0011】

【発明が解決しようとする課題】ところで、上記高分子分散型液晶素子の液晶／高分子複合膜6の光散乱性は、この複合膜6中の液晶溜まり（液晶8が閉じ込められている部分）の大きさおよび分布状態（単位体積当たりの分布数）によって異なるため、良好な光散乱性をもつ複合膜6を形成するには、混合溶液への光の照射を、高分子材料が適度な大きさおよび分布状態の液晶だまりを形成して光重合するように照射光量を選んで行なうことが望まれる。

【0012】しかし、従来の高分子分散型液晶素子の製造方法では、混合溶液への照射光のうちのかんりの量の光が二色性染料によって吸収されてしまうため、混合溶液への照射光を効率よく高分子材料の光重合に利用することができなかった。

【0013】このため、従来は、混合溶液への照射光量を、二色性染料での光吸収を見込んである程度多くして

いるが、混合溶液への照射光量を多くすると、二色性染料に吸収される光量も多くなって二色性染料が劣化してしまうため、照射光量をむやみに多くすることには問題があり、したがって、従来の製造方法では、高分子材料を適度な大きさおよび分布状態の液晶だまりを形成するように光重合させて良好な光散乱性をもつ液晶／高分子複合膜を形成することはできなかった。

【0014】この発明は、混合溶液への照射光を効率よく高分子材料の光重合に利用して、混合溶液への照射光量を多くすることなく良好な光散乱性をもつ液晶／高分子複合膜を形成することができる、高分子分散型液晶素子の製造方法を提供することを目的としたものである。

【0015】

【課題を解決するための手段】この発明の高分子分散型液晶素子の製造方法は、一対の基板間もしくは一方の基板上に、光により重合反応する高分子材料と二色性染料を含む液晶との混合溶液の層を設け、その二色性染料の分子を所定方向にほぼ一様に配向させた状態で、前記混合溶液に、偏光板を介して、次の1，2，3のいずれかの条件で光を照射し、前記高分子材料を光重合させて液晶／高分子複合膜を形成することを特徴とするものである。

【0016】【条件1】前記二色性染料の分子長軸方向の吸収軸に対して直交する方向と前記偏光板を透過した直線偏光の偏光方向とのなす角 $\phi$ と、前記偏光板の透過率 $x$ とが、

$$x > (\pi/2) \sin \phi$$

を満たし、かつ、前記二色性染料の二色性比 $\kappa$ が、

$$\kappa > (x - \cos \phi) / (\sin \phi - 2x/\pi)$$

であること。

【0017】【条件2】前記二色性染料の分子長軸方向の吸収軸に対して直交する方向と前記偏光板を透過した直線偏光の偏光方向とのなす角 $\phi$ と、前記偏光板の透過率 $x$ とが、

$$x > [\pi / (\pi + 2)] (\sin \phi + \cos \phi)$$

を満たし、かつ、前記二色性染料の二色性比 $\kappa$ が、

$$\kappa < (x - \cos \phi) / (\sin \phi - 2x/\pi)$$

であること。

【0018】【条件3】前記二色性染料の分子長軸方向の吸収軸に対して直交する方向と前記偏光板を透過した直線偏光の偏光方向とのなす角 $\phi$ と、前記偏光板の透過率 $x$ とが、

$$x \geq (\pi/2) \sin \phi$$

$$x \geq [\pi / (\pi + 2)] (\sin \phi + \cos \phi)$$

を満たすこと。

【0019】なお、上記混合溶液に照射する光は、所定方向にほぼ一様に配向された二色性染料の分子長軸方向の吸収軸に対してほぼ垂直な方向から入射させるのが望ましい。また、上記1，2，3の条件は、いずれも、二色性染料が、正の二色性を有するp型の二色性染料であ

る場合に成立する。

#### 【0020】

【作用】このように、光により重合反応する高分子材料と二色性染料を含む液晶との混合溶液の層の二色性染料の分子を所定方向にほぼ一様に配向させておき、その状態で前記混合溶液に、偏光板を介して、上記1, 2, 3のいずれかの条件で光を照射すると、二色性染料による光吸収が少なくなり、相対的に高分子材料に照射される光を多くさせ、相対的に二色性染料による光吸収を少なくさせる。

【0021】このため、この発明の製造方法によれば、混合溶液への照射光を効率よく高分子材料の光重合に利用して、混合溶液への照射光量を多くすることなく良好な光散乱性をもつ液晶／高分子複合膜を形成することができるとともに、二色性染料の光吸収による劣化を抑制することもできる。

#### 【0022】

【実施例】以下、この発明の一実施例を図1～図9を参照して説明する。図1は一对の基板間に設けた混合溶液に光を照射している状態の断面図であり、この実施例では、次のようにして高分子分散型液晶素子を製造する。

【0023】まず、表示用の透明電極13, 14を設けた一对の透明基板（例えばガラス基板）11, 12の電極形成面上にそれぞれ、液晶の分子および二色性染料の分子を一方向に配向させる配向処理を施す。

【0024】この配向処理は、例えば、基板11, 12上にポリイミド等からなる水平配向膜14, 15を形成し、その膜面を一方向にラビングすることによって行なう。なお、上基板11側の配向膜14と、下基板12側の配向膜15とは互いに平行でかつ逆方向にラビングする。

【0025】次に、上記配向処理を施した一对の基板11, 12をその電極形成面を互に対向させて配置し、この両基板11, 12の外周縁部を図示しないシール材を介して接合して液晶素子を組立てる。なお、この液晶素子は例えば単純マトリックス型のものであり、図において下基板12側の電極14は走査電極、上基板11側の電極13は信号電極である。

【0026】次に、上記両基板11, 12間の前記シール材で囲まれた領域に、前記シール材の一部を欠落させて形成しておいた注入口から、光によって重合反応する高分子材料と二色性染料を含む液晶21との混合溶液20を真空注入法により充填して、基板11, 12間に前記混合溶液20の層を設ける。

【0027】なお、前記液晶21には例えば誘電異方性が正のネマティック液晶を用い、この液晶21に添加する二色性染料には、正の二色性を有するp型の二色性染料を用いる。

【0028】このp型の二色性染料は、その分子の長軸方向に光吸収の遷移モーメントを有するものであり、分

子長軸方向の吸収軸と、それに対して直交する方向とのうち、分子長軸方向の吸収軸に沿う偏光成分の光の吸光度が、前記直交する方向に沿う偏光成分の光の吸光度よりも常に大きいという特性をもっている。

【0029】なお、上記二色性染料は、二色性液晶染料（可視光域中のある波長域の光を吸収する特性をもった着色液晶）、例えば、赤橙色のアゾ系液晶染料、黄色のアゾキシ系液晶染料等であってもよい。

【0030】上記混合溶液20を両基板11, 12間に充填すると、この混合溶液20中の液晶21の液晶分子21aおよび二色性染料の分子21bが、両基板11, 12の配向膜15, 16に施されている配向処理により、図1に示したように、基板11, 12面（配向膜15, 16面）に対し若干チルトした状態で、前記配向処理の方向にほぼ一様に配向する。

【0031】この後は、両基板11, 12間の混合溶液20に、一方の基板、例えば上基板11の外側から、偏光板17を介して、後述する条件で光（紫外線）を照射し、前記高分子材料を光重合させて液晶／高分子複合膜を形成する。

【0032】このように、上記混合溶液20に光を照射すると、混合溶液20の高分子材料が光により重合反応し、液晶21が二色性染料とともに相分離して、液晶／高分子複合膜が形成される。

【0033】図2は上記のようにして製造された高分子分散型液晶素子の断面図であり、形成された液晶／高分子複合膜22は、スポンジのような断面をもつようにポリマー化した高分子層23の各隙間部に、二色性染料を含む液晶21が閉じ込められた構造をなしている。

【0034】なお、この液晶素子の両基板11, 12には配向処理が施されているが、上記高分子材料を光重合させて複合膜22を形成すると、高分子層23の各隙間部に二色性染料を含む液晶21が閉じ込められるため、配向膜15, 16に施した配向処理による配向規制力が液晶21に及ばなくなり、液晶分子21aおよび染料分子21bが図2のようなランダムな配向状態になる。

【0035】ただし、上記複合膜22には、液晶21が配向膜15, 16に接している部分もあるため、その部分では、配向膜15, 16上の液晶分子21aおよび染料分子21bが前記配向処理の方向に配向した状態になるが、このような配向状態は、複合膜22と配向膜15, 16との界面付近にできるだけであり、複合膜22全体で見れば、そのほとんどの領域において液晶分子21aおよび染料分子21bがランダムな配向状態になる。

【0036】また、図1に示した偏光板17は、上記高分子分散型液晶素子の製造において混合溶液20に光を照射する際に用いられるものであり、製造された高分子分散型液晶素子には偏光板はない。

【0037】次に、上記高分子分散型液晶素子の製造に

における混合溶液 20 への光の照射条件を説明する。図 3 は、上記混合溶液 20 中の染料分子 21 b の吸収軸と上記偏光板 17 を透過した直線偏光の偏光方向とを光の照射方向（混合溶液 20 の層に対してほぼ垂直な方向）から見た図であり、図において、 $L_P$  は二色性染料の分子長軸方向の吸収軸、 $L_H$  は前記分子長軸方向の吸収軸  $L_P$  に対して直交する方向の軸（以下、短軸方向の軸という）、 $\phi$  は二色性染料の短軸方向の軸  $L_H$  と偏光板 17 を透過した直線偏光の偏光方向とのなす角を示している。

【0038】そして、上記混合溶液 20 の層への光の照射は、次の 1, 2, 3 のいずれかの条件で行なう。

【条件 1】上記二色性染料の短軸方向の軸  $L_H$  と偏光板 17 を透過した直線偏光の偏光方向とのなす角  $\phi$  と、前記偏光板 17 の透過率  $\chi$  とが、

$$\chi > (\pi/2) \sin \phi$$

を満たし、かつ、前記二色性染料の二色性比  $\kappa$  が、

$$\kappa > (\chi - \cos \phi) / (\sin \phi - 2\chi/\pi)$$

であること。

【0039】【条件 2】上記二色性染料の短軸方向の軸  $L_H$  と偏光板 17 を透過した直線偏光の偏光方向とのなす角  $\phi$  と、前記偏光板 17 の透過率  $\chi$  とが、

$$\chi > [\pi / (\pi + 2)] (\sin \phi + \cos \phi)$$

を満たし、かつ、前記二色性染料の二色性比  $\kappa$  が、

$$\kappa < (\chi - \cos \phi) / (\sin \phi - 2\chi/\pi)$$

であること。

【0040】【条件 3】上記二色性染料の短軸方向の軸  $L_H$  と偏光板 17 を透過した直線偏光の偏光方向とのなす角  $\phi$  と、前記偏光板 17 の透過率  $\chi$  とが、

$$\chi \geq (\pi/2) \sin \phi$$

$$\chi \geq [\pi / (\pi + 2)] (\sin \phi + \cos \phi)$$

を満たすこと。

【0041】なお、図 3 に示したように、染料分子 21 b の長軸方向吸収軸  $L_P$  は、分子長軸  $O$  に対して若干斜めにずれており、染料分子 21 b は配向膜 15, 16 の配向処理方向に分子長軸  $O$  が向いた状態で配向するため、上記偏光板 17 の透過軸の向き、つまり混合溶液 20 に入射させる直線偏光の偏光方向は、前記配向処理方向に、染料分子 21 b の長軸  $O$  と長軸方向吸収軸  $L_P$  とのずれ角を加味して設定する。

【0042】また、上記混合溶液 20 に照射する光は、所定方向にほぼ一様に配向された二色性染料の分子長軸方向の吸収軸  $L_P$  に対してほぼ垂直な方向から入射させるのが望ましい。ただし、基板 11, 12 面に対する染料分子 21 b のチルト角は極く小さいため、照射光は、基板 11, 12 面に対してほぼ垂直な方向から入射させてもよい。

【0043】このように、光により重合反応する高分子材料と二色性染料を含む液晶との混合溶液 20 の層の二色性染料の分子 21 b を所定方向にほぼ一様に配向させ

ておき、その状態で前記混合溶液に、偏光板 17 を介して、上記 1, 2, 3 のいずれかの条件で光を照射すると、高分子材料に照射される光量が多くなり、相対的に、二色性染料による光吸収が少なくなる。

【0044】このため、この製造方法によれば、混合溶液 20 への照射光を効率よく高分子材料の光重合に利用して、混合溶液 20 への照射光量を多くすることなく良好な光散乱性をもつ液晶／高分子複合膜 22 を形成することができる。

【0045】すなわち、上記製造方法における二色性染料の光吸収を、従来の製造方法と比較して説明すると、従来の製造方法では、混合溶液中の二色性染料の分子がランダムな方向を向いている状態で前記混合溶液に無偏光の光を照射しているため、各染料分子の光吸収は、その染料分子の向きによって異なる。

【0046】図 4 は従来の製造方法における混合溶液中の染料分子の向きを示しており、基板面に対して垂直な方向から混合溶液に光を照射したときの各染料分子の光吸収量は、二色性染料の分子長軸方向の吸収軸  $L_P$  に沿う偏光成分の光に対する吸収度を  $A_P$ 、短軸方向の軸  $L_H$  に沿う偏光成分の光に対する吸収度を  $A_H$  とすると、次の通の式で表される。

【0047】基板面に対してある角度  $\theta$  で斜めに傾いている染料分子の 1 分子当たりの光吸収量は、

$$A_P \cos \theta + A_H$$

である。

【0048】したがって、基板面に対する傾き角が  $0^\circ$ （基板面と平行）、すなわち  $\theta = 0^\circ$  のときの染料分子の 1 分子当たりの光吸収量は、最大値

$$A_P + A_H \text{（吸収量最大）}$$

となり、また、基板面に対する傾き角が  $90^\circ$ （基板面に垂直）、すなわち  $\theta = 90^\circ$  のときの染料分子の 1 分子当たりの光吸収量は、最小値

$$A_H \text{（吸収量最少）}$$

となる。

【0049】そして、傾き角がランダムな染料分子のうち所定角  $\theta$  の染料分子の存在比は、 $\theta$  の値によらずほぼ一定であるので、従来の製造方法における混合溶液中の二色性染料の吸光量の平均値は、

【0050】

【数 1】

$$\frac{\int_0^{\pi/2} (A_P \cos \theta + A_H) d\theta}{\pi/2}$$

$$= 2/\pi A_P + A_H \quad \cdots (1)$$

となる。

【0051】一方、上記実施例の製造方法では、混合溶液中の染料分子 21 b を所定方向にほぼ一様に水平配向させた状態で、前記混合溶液に、直線偏光させた光を照

射しているため、図3のように染料分子21bの短軸方向の吸収軸 $L_H$ に対して角度 $\phi$ ずれた偏光方向の直線偏光を照射したときの二色性染料の1分子当たりの吸光量は、

$$A_P \sin \phi + A_H \cos \phi \quad \cdots (2)$$

となる。

【0052】次に、上記実施例の製造方法において高分子材料に照射される光の強度を、従来の製造方法と比較して説明すると、図5は、上記実施例の製造方法における高分子材料への光照射経路と、従来の製造方法における高分子材料への光照射経路とを示す模式図であり、

(a)は実施例の製造方法における光照射経路、(b)は従来の製造方法における光照射経路を示している。

【0053】この図5のように、光源ランプからの光の強度比を $P$ (単位 $W$ )とし、従来の製造方法における高分子材料への照射光の強度比を $P1$ 、実施例の製造方法における高分子材料への照射光の強度比を $P2$ とすると、従来の製造方法では、二色性染料の吸光量の平均値が上記式(1)で表される値であるため、高分子材料への照射光の強度比 $P1$ を、

$$P1 = P / [ (2/\pi) A_P + A_H ]$$

とすれば、上記実施例の製造方法では、光源ランプからの光のうち、偏光板を透過した光だけが混合溶液に入射するが、二色性染料の吸光量が上記式(2)で表される値であるため、偏光板を透過した光の強度を $\chi P$ とすると、高分子材料への照射光の強度比 $P2$ は、

$$P2 = \chi P / (A_P \sin \phi + A_H \cos \phi)$$

と表すことができる。

【0054】すなわち、従来の製造方法における高分子材料への照射光の強度比 $P1$ と、実施例の製造方法における高分子材料への照射光の強度比 $P2$ との比 $P1 : P2$ は、

$$P / [ (2/\pi) A_P + A_H ] : \chi P / (A_P \sin \phi + A_H \cos \phi) \quad \cdots (3)$$

である。

【0055】そして、

$$P2 / P1 > 1 \quad \cdots (4)$$

であれば、つまり、実施例の製造方法における高分子材料への照射光の強度 $P2$ が、従来の製造方法における高分子材料への照射光の強度 $P1$ より大きければ、実施例の製造方法の方が従来の製造方法に比べて、高分子材料に照射される光量を多くできる。

【0056】したがって、光源ランプからの光を効率よく高分子材料の光重合に利用できる条件は、上記式(3)と式(4)より、

$$\chi [ (2/\pi) A_P + A_H ] / (A_P \sin \phi + A_H \cos \phi) > 1 \quad \cdots (5)$$

となる。

【0057】そして、二色性染料の吸収度 $A_P$ 、 $A_H$ はいずれも正の値( $A_P > 0$ 、 $A_H > 0$ )であり、また、

二色性染料の短軸方向の吸収軸 $L_H$ と偏光板17を透過した直線偏光の偏光方向とのなす角 $\phi$ は $0^\circ \sim 90^\circ$ の範囲( $0^\circ \leq \phi \leq 90^\circ$ )であって、 $\sin \phi \geq 0$ 、 $\cos \phi \geq 0$ であるから、上記式(5)を展開すると、

$$A_P \sin \phi + A_H \cos \phi < \chi [ (2/\pi) A_P + A_H ]$$

よって、

$$A_P (\sin \phi - 2\chi/\pi) + A_H (\cos \phi - \chi) < 0$$

…(6)

となる。

【0058】すなわち、上記式(6)を満たせば、光源ランプの光量を増大することなく、高分子材料に、より多くの光量を照射することができる。ところで、二色性染料の吸収度 $A_P$ 、 $A_H$ はいずれも正の値であるが、 $\sin \phi - (2\chi/\pi)$ と $\cos \phi - \chi$ の値は、次の(I)～(IV)のいずれかである。

【0059】

(I)  $\sin \phi - (2\chi/\pi) \leq 0$  かつ  $\cos \phi - \chi < 0$

または  $\sin \phi - (2\chi/\pi) < 0$  かつ  $\cos \phi - \chi \leq 0$

(II)  $\sin \phi - (2\chi/\pi) > 0$  かつ  $\cos \phi - \chi < 0$

(III)  $\sin \phi - (2\chi/\pi) < 0$  かつ  $\cos \phi - \chi > 0$

(IV)  $\sin \phi - (2\chi/\pi) \geq 0$  かつ  $\cos \phi - \chi > 0$

または  $\sin \phi - (2\chi/\pi) > 0$  かつ  $\cos \phi - \chi \geq 0$

上記(I)～(IV)の各場合についてみると、 $\sin \phi - (2\chi/\pi)$ と $\cos \phi - \chi$ が上記(I)の関係にある場合、上記式(6)は、

$$A_P / A_H \geq (\chi - \cos \phi) / (\sin \phi - 2\pi/\pi)$$

…(7)

となる。

【0060】ところで、上記式(7)の右辺の分母が $\sin \phi - (2\chi/\pi) = 0$ のとき、分子が $\chi - \cos \phi > 0$ であれば、上記式(6)は、 $A_P / A_H$ がどのような値でも、つまり、いかなる吸収度の二色性染料においても成立する。

【0061】また、式(7)の右辺の分子の $\chi - \cos \phi$ が0のとき、分子が $\sin \phi - (2\chi/\pi) < 0$ であれば、上記式(6)は、 $A_P / A_H$ がどのような値でも、つまり、いかなる吸収度の二色性染料においても成立する。

【0062】したがって、残る条件は、 $\chi - \cos \phi > 0$ で、かつ、 $\sin \phi - (2\chi/\pi) < 0$ のときであるが、このとき、

$$(\chi - \cos \phi) / (\sin \phi - 2\chi/\pi) = a(\chi, \phi)$$

とすると、

$$a(\chi, \phi) \leq 0 \quad \cdots (8)$$

となる。

【0063】上記実施例で用いた二色性染料は、p型染料、すなわち二色性比 $\kappa$ ( $\kappa = A_P / A_H$ )が常に1より大きい染料であるため、 $A_P / A_H$ の値は常に1より大、つまり、

$$A_P / A_H > 1 \quad \cdots (9)$$

となるので、上記式(7)および式(8)は、 $\chi$ 、 $\phi$ の値に

かわらず、常に式(9)を満たす。

【0064】いいかえれば、二色性染料の二色性比  $\kappa$  が1より大であれば、その  $A_P / A_H$  の値がどのような二色性染料であっても、上記式(7)は、 $\chi$ ,  $\phi$  の値にかかわらず成立する。

【0065】したがって、(I)の場合、つまり  $\sin\phi - (2\chi/\pi) \leq 0$  かつ  $\cos\phi - \chi < 0$ 、または  $\sin\phi - (2\chi/\pi) < 0$  かつ  $\cos\phi - \chi \leq 0$  のときは、二色性染料がどのような二色性比  $\kappa$  をもつ染料であっても、従来の製造方法に比べて、高分子材料に照射される光量が多くなり、相対的に、二色性染料による光吸収が少なくなる。

【0066】また、 $\sin\phi - (2\chi/\pi)$  と  $\cos\phi - \chi$  が上記(II)の関係にある場合、上記式(6)は、 $A_P / A_H < a(\chi, \phi)$  …(10) となる。

【0067】ここで、二色性染料の  $A_P / A_H$  の値は  $A_P / A_H > 1$  であるため、上記式(10)が成立するには、 $a(\chi, \phi)$  が最低でも1より大であること、つまり、 $1 < a(\chi, \phi)$  …(11) であることが条件となる。

【0068】式(10)より、式(11)は、 $\chi > [\pi / (\pi + 2)] (\sin\phi + \cos\phi)$  …(12) となる。

【0069】このため、(II)の場合は、上記式(10)と式(12)を同時に満足することが必要であり、したがって、 $\sin\phi - (2\chi/\pi) > 0$  かつ  $\cos\phi - \chi < 0$  のときは、二色性染料の  $A_P / A_H$  の値が  $A_P / A_H < a(\chi, \phi)$  であるときに、従来の製造方法に比べて、高分子材料に照射される光量が多くなり、相対的に、二色性染料による光吸収が少なくなる。

【0070】また、 $\sin\phi - (2\chi/\pi)$  と  $\cos\phi - \chi$  が上記(III)の関係にある場合、上記式(6)は、 $A_P / A_H > a(\chi, \phi)$  …(13) となる。

【0071】ここで、 $a(\chi, \phi)$  が1以下、つまり、 $1 \geq a(\chi, \phi)$  …(14) であれば、 $A_P / A_H$  がどのような値 (ただし  $A_P / A_H > 1$ ) でも、上記式(13)は成立する。

【0072】式(13)より、式(14)は、 $\chi \geq [\pi / (\pi + 2)] (\sin\phi + \cos\phi)$  …(15) となる。

【0073】したがって、(III)の場合、つまり  $\sin\phi - (2\chi/\pi) < 0$  かつ  $\cos\phi - \chi > 0$  のときは、 $1 \geq a(\chi, \phi)$  であれば、二色性染料がどのような二色性比  $\kappa$  をもつ染料であっても、従来の製造方法に比べて、高分子材料に照射される光量が多くなり、相対的に、二色性染料による光吸収が少なくなる。

【0074】さらに、(III)の場合、 $1 < a(\chi, \phi)$  …(16)

のときでも、

$$A_P / A_H > a(\chi, \phi) \quad \dots(17)$$

であれば、上記式(13)は成立する。

【0075】その場合、上記式(16)は、 $\chi < [\pi / (\pi + 2)] (\sin\phi + \cos\phi)$  …(18) となる。

【0076】このため、(III)の場合であって、 $1 < a(\chi, \phi)$  であるときは、二色性染料の  $A_P / A_H$  の値が  $A_P / A_H > a(\chi, \phi)$  で、かつ  $\chi < [\pi / (\pi + 2)] (\sin\phi + \cos\phi)$  あるときに、従来の製造方法に比べて、高分子材料に照射される光量が多くなり、相対的に、二色性染料による光吸収が少なくなる。

【0077】一方、 $\sin\phi - (2\chi/\pi)$  と  $\cos\phi - \chi$  が上記(IV)の関係にある場合は、上記式(6)は成立しない。以上をまとめると、従来の製造方法よりも混合溶液への照射光を効率よく高分子材料の光重合に利用できる効果が得られるのは、 $0 < \chi < 1$ ,  $0 \leq \phi \leq \pi/2$ ,  $A_P > 0$ ,  $A_H > 0$ ,  $A_P / A_H > 1$  において、イ.  $\chi \geq \pi/2 \sin\phi$ ,  $\chi \geq \cos\phi$  で、 $A_P / A_H$  の値は問わない。

【0078】ロ.  $\chi < \pi/2 \sin\phi$ ,  $\chi > [\pi / (\pi + 2)] (\sin\phi + \cos\phi)$  で、かつ、 $A_P / A_H < (\chi - \cos\phi) / (\sin\phi - 2\chi/\pi)$   
ハ.  $\chi > \pi/2 \sin\phi$ ,  $\chi \geq [\pi / (\pi + 2)] (\sin\phi + \cos\phi)$  で、 $A_P / A_H$  の値は問わない。

【0079】ニ.  $\chi < \cos\phi$ ,  $\chi < [\pi / (\pi + 2)] (\sin\phi + \cos\phi)$  で、かつ、 $A_P / A_H > (\chi - \cos\phi) / (\sin\phi - 2\chi/\pi)$  である。

【0080】図6は、横軸に二色性染料の短軸方向の吸収軸  $L_H$  と偏光板17を透過した直線偏光の偏光方向とのなす角  $\phi$  をとり、縦軸に前記偏光板17の透過率  $\chi$  をとって、上記条件イ、ロ、ハ、ニの  $\phi$  と  $\chi$  の範囲を示した図である。

【0081】ここで、上記条件イ+ハ+ニは、 $\phi$  と  $\chi$  の範囲および二色性比において、上述した「条件1」を含有している。すなわち、図7では上記「条件1」における  $\phi$  と  $\chi$  の範囲を示しており、図において斜線を施した領域が条件イ+ハ+ニに含まれている。なお、この領域は、 $\phi = 0$  の線上を含むが、 $\chi = 1$  および  $\chi = (\pi/2) \sin\phi$  の線上は含まない。

【0082】そして、上記条件イ、ハ、ニの  $\phi$  と  $\chi$  の範囲のうち、条件イとハは  $A_P / A_H$  の値を問わない範囲であるのに対して、条件ニは  $A_P / A_H > (\chi - \cos\phi) / (\sin\phi - 2\chi/\pi)$  であることを条件とする範囲であるが、上記「条件1」のように、二色性染料の二色性比  $\kappa$  ( $\kappa = A_P / A_H$ ) が  $\kappa > (\chi - \cos\phi) / (\sin\phi - 2\chi/\pi)$  であれば、 $\phi$  と  $\chi$  の値が条件イ、ハ、ニのいずれの範囲であっても、上述した効果が得られる。

【0083】一方、上記条件イ、ロ、ハ、ニのうち、条

件イ+ロ+ハは、 $\phi$ と $\chi$ の値および二色性比において、上述した〔条件2〕を含有している。図8は上記〔条件2〕における $\phi$ と $\chi$ の範囲を示しており、図において斜線を施した領域が条件イ+ロ+ハに含まれている。なお、この領域は、 $\phi=0$ および $\phi=\pi/2$ の線上を含み、 $\chi=1$ および $\chi=[\pi/(\pi+2)]$  ( $\sin\phi+\cos\phi$ )の線上は含まない。

【0084】そして、上記条件イ、ロ、ハの $\phi$ と $\chi$ の範囲のうち、条件イとハは $A_P/A_H$ の値を問わない範囲であるのに対して、条件ロは $A_P/A_H < (\chi - \cos\phi) / (\sin\phi - 2\chi/\pi)$ であることを条件とする範囲であるが、上記〔条件2〕のように、二色性染料の二色性比 $\kappa$  ( $\kappa=A_P/A_H$ ) が $\kappa < (\chi - \cos\phi) / (\sin\phi - 2\chi/\pi)$ であれば、 $\phi$ と $\chi$ の値が条件イ、ロ、ハのいずれの範囲であっても、上述した効果が得られる。

【0085】さらに、上記条件イ、ロ、ハ、ニのうち、条件イとハは、 $\phi$ と $\chi$ の値が $A_P/A_H$ の値を問わない範囲である点で共通している。そこで、この条件イとハを1つの範囲としてみると、その範囲は、上述した〔条件3〕、つまり、

$$\chi \geq (\pi/2) \sin\phi$$

と、

$$\chi \geq [\pi/(\pi+2)] (\sin\phi + \cos\phi)$$

との両方を満たす範囲である。

【0086】図9は上記〔条件3〕における $\phi$ と $\chi$ の範囲を示しており、上記条件イ、ハの $\phi$ と $\chi$ の値は図9の斜線を施した領域内にある。なお、この領域は、 $\chi = (\pi/2) \sin\phi$ および $\chi = [\pi/(\pi+2)] (\sin\phi + \cos\phi)$ の線上と $\phi=0$ の線上を含み、 $\chi=1$ の線上は含まない。ただし、 $\chi = (\pi/2) \sin\phi$ と、 $\chi = [\pi/(\pi+2)] (\sin\phi + \cos\phi)$ との2つの式は同時には成立しないため、前記領域には、 $\chi = (\pi/2) \sin\phi$ の線と、 $\chi = [\pi/(\pi+2)] (\sin\phi + \cos\phi)$ の線との交点は含まれない。

【0087】そして、上記条件イとハの $\phi$ と $\chi$ の範囲は、いずれも $A_P/A_H$ の値を問わない範囲であるため、上記〔条件3〕では、二色性染料の二色性比 $\kappa$  ( $\kappa=A_P/A_H$ ) がどのような値であっても、上述した効果が得られる。

【0088】このように、上記製造方法は、上記〔条件1〕、〔条件2〕、〔条件3〕のいずれによっても、混合溶液20への照射光を効率よく高分子材料の光重合に利用することができるのであり、したがって、混合溶液20への照射光量を多くすることなく、良好な光散乱性をもつ液晶/高分子複合膜22を形成することができる。

【0089】なお、上記実施例では、一對の基板11、12をシール材を介して接合して液晶素子を組立てた後に、両基板11、12間に混合溶液20を注入充填し

て、その混合溶液20への光照射により液晶/高分子複合膜22を形成しているが、前記複合膜は、液晶素子を組立てる前に一方の基板上に形成してもよい。

【0090】その場合は、一方の基板の上に、液晶の分子および二色性染料の分子を一方向に配向させる配向処理を施した後、この一方の基板上に混合溶液を塗布して混合溶液層を設け、この混合溶液に上記〔条件1〕、

〔条件2〕、〔条件3〕のいずれかで光を照射して液晶/高分子複合膜を形成し、その後、前記複合膜の上に他方の基板（例えば樹脂フィルムからなる基板）を設けて液晶素子を組立てればよい。

【0091】

【発明の効果】この発明の高分子分散型液晶素子の製造方法は、一對の基板間もしくは一方の基板上に、光により重合反応する高分子材料と二色性染料を含む液晶との混合溶液の層を設け、その二色性染料の分子を所定方向にほぼ一様に配向させた状態で、前記混合溶液に、偏光板を介して、前記二色性染料の分子長軸方向の吸収軸に対して直交する方向と前記偏光板を透過した直線偏光の偏光方向とのなす角 $\phi$ と、前記偏光板の透過率 $\chi$ とが、 $\chi > (\pi/2) \sin\phi$ を満たし、かつ、前記二色性染料の二色性比 $\kappa$ が、 $\kappa > (\chi - \cos\phi) / (\sin\phi - 2\chi/\pi)$ である条件、または、前記 $\phi$ と $\chi$ とが、 $\chi > [\pi/(\pi+2)] (\sin\phi + \cos\phi)$ を満たし、かつ、前記二色性染料の二色性比 $\kappa$ が、 $\kappa < (\chi - \cos\phi) / (\sin\phi - 2\chi/\pi)$ である条件、または、前記 $\phi$ と $\chi$ とが、 $\chi \geq (\pi/2) \sin\phi$ と $\chi \geq [\pi/(\pi+2)] (\sin\phi + \cos\phi)$ とを満たす条件、で光を照射し、前記高分子材料を光重合させて液晶/高分子複合膜を形成するものであるから、前記混合溶液への照射光を効率よく高分子材料の光重合に利用して、混合溶液への照射光量を多くすることなく良好な光散乱性をもつ液晶/高分子複合膜を形成することができる。

【図面の簡単な説明】

【図1】この発明の一実施例を示す、一對の基板間に設けた混合溶液に光を照射している状態の断面図。

【図2】製造された高分子分散型液晶素子の断面図。

【図3】混合溶液中の染料分子の吸収軸と偏光板を透過した直線偏光の偏光方向とを光の照射方向から見た図。

【図4】従来の製造方法における混合溶液中の染料分子の向きを示す図。

【図5】実施例の製造方法における高分子材料への光照射経路と、従来の製造方法における高分子材料への光照射経路とを示す模式図。

【図6】従来の製造方法よりも混合溶液への照射光を効率よく高分子材料の光重合に利用できる $\phi$ と $\chi$ の範囲を示す図。

【図7】〔条件1〕における $\phi$ と $\chi$ の範囲を示す図。

【図8】〔条件2〕における $\phi$ と $\chi$ の範囲を示す図。

【図9】〔条件3〕における $\phi$ と $\chi$ の範囲を示す図。



【図10】従来の高分子分散型液晶素子の断面図。

【図11】図10の一部分の拡大図。

【符号の説明】

11, 12…基板

13, 14…電極

15, 16…配向膜

17…偏光板

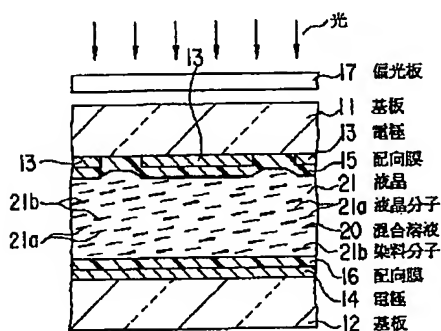
20…混合溶液

21…液晶

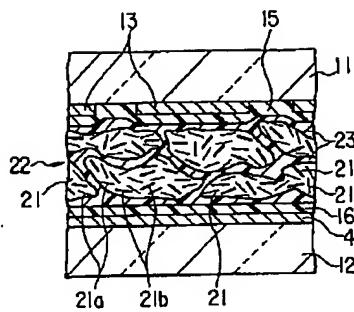
21a…液晶分子

21b…二色性染料の分子

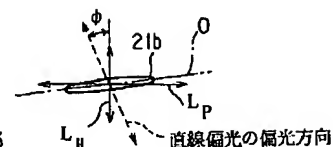
【図1】



【図2】



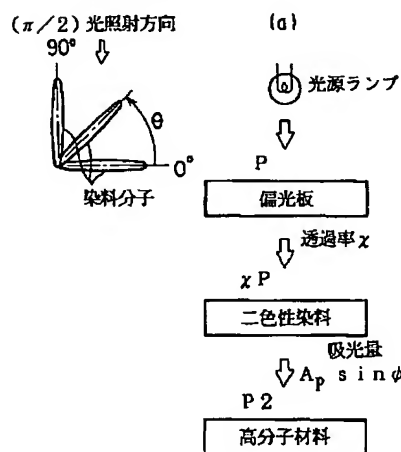
【図3】



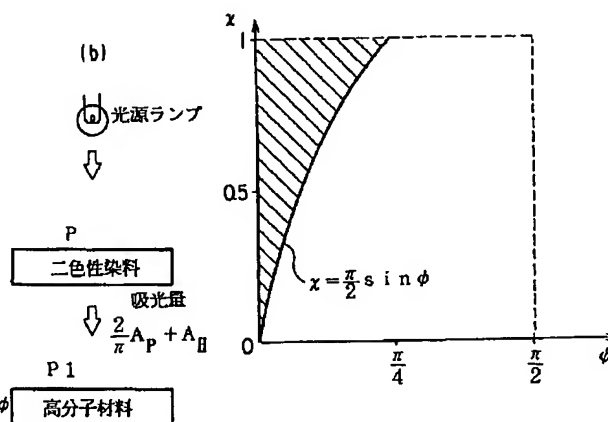
【図7】

【図4】

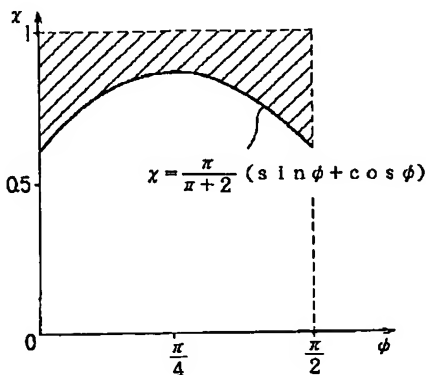
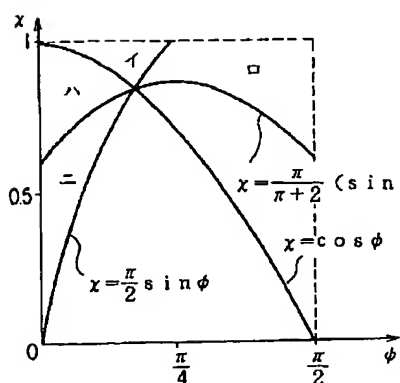
【図5】



【図6】

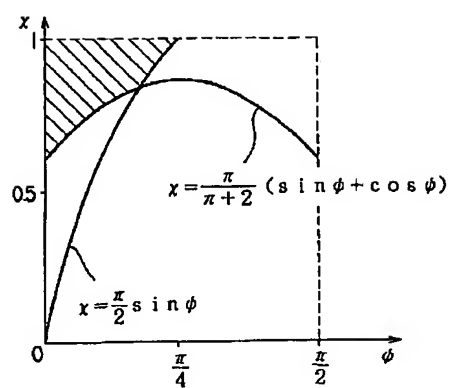


【図8】

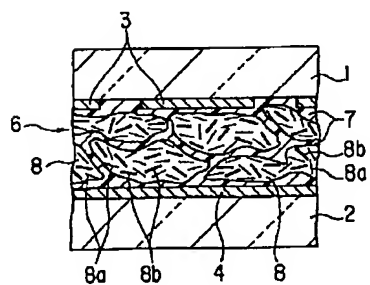




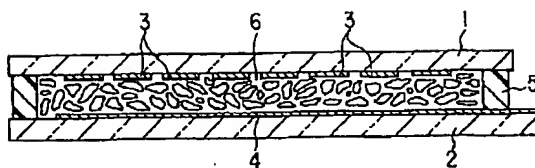
【図9】



【図11】



【図10】



## ORIENTED DISPERSION OF LIQUID CRYSTAL DROPLETS IN A POLYMER MATRIX WITH LIGHT INDUCED ANISOTROPY

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 p. 295-299 = 5

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A new method to form aligned liquid crystal droplets in a polymer matrix is proposed. A mutual orientation of droplet optical axis is caused by light-induced anisotropy in a polymer matrix. The influence of temperature and electric field on anisotropic properties of the system is observed and discussed.

### INTRODUCTION

Investigations of liquid crystals (LC), dispersed in a polymer matrix are steady developing.<sup>1</sup> They are of interest for two reasons. First, polymer dispersed liquid crystals (PDLC) form a new class of heterogeneous systems with a very developed surface and many new effects have already been discovered and still to be anticipated in future. Second, PDLC present materials perspective for fast large area flexible displays.

Nematic PDLC displays are mostly developed. This type of displays provides a reversible field induced transition from an opaque state to the transparent one. The mechanism of the switching is caused by electrically controlled refractive index matching of LC and polymer matrix.

It has been outlined<sup>2</sup> that characteristics of the opaque-transparent transition should be strongly dependent on a mutual orientation of the director in separate LC droplets. Indeed, the light scattering depends on the optical axis orientation with respect to the light polarization vector  $E$ . Therefore, the characteristics of transmitted, reflected and scattered light should be different for oriented and randomly arranged LC droplet dispersion.

Recently oriented LC droplets were obtained under the action of external electric or magnetic field on cooling the system heated previously up to the plastic state.<sup>2,3</sup> This method does not permit one to obtain the steady state system. The alignment deteriorates spontaneously after field switching off.

In the papers<sup>4,5</sup> oriented dispersions were formed by stretching the polymer film

with randomly oriented LC droplets. In this case LC droplets are extended in the direction of stretching.

In the present communications a new method to form aligned PDLC films is reported. We propose to use material with light induced anisotropy as a matrix. Some preliminary experimental results on film characteristics are presented.

## EXPERIMENTAL

The modified polyvinylcinnamate (PVCN) synthesized from intermediate products of "Fluka" was taken as a material with light induced anisotropy. In this type of polymer, the anisotropy results from the occurrence of orientationally ordered chemical links between polymer chains under the action of polarized UV light.<sup>6</sup> We have recently shown that in films of this material the nematic alignment is planar with the easy axis directly perpendicularly to the light vector  $E_{uv}$ .<sup>7</sup> Thus, we hoped that UV illumination of the system would lead to the ordering of the LC droplets. Unfortunately, LC molecules dissolved in a PVCN matrix inhibited the photochemical reaction mentioned.

The oriented dispersion was obtained as follows. The emulsion of PVCN dissolved in dichlorobenzene and a fluid (which is not soluble in the solvent for PVCN) was prepared with a shaker. Then the emulsion was spread onto a glass substrate and dried. In the case of water, a rigid polymer matrix with pores filled with water was produced.

The glass plate with the layer was inserted into a vacuum chamber and water was removed. Then it was put in a vessel with nematic pentylcyanobiphenyl (clearing point  $T_c \cong 32^\circ\text{C}$ ). Subsequently this system was illuminated by polarized UV light of a Hg lamp (the lamp power  $P_{ex} \cong 10\text{ mW}$ , exposure time  $t_{ex} \cong 30\text{ min}$ , the diameter of light spot in the plane of the film  $d_{ex} \cong 10\text{ mm}$ ). Optical birefringence points to the light induced anisotropy of the porous matrix.

The oriented dispersion could be also obtained without preliminary removal of water. We noticed that water is expelled by LC, if the polymer is put into the LC and air is pumped out of the chamber.

A dispersion obtained is shown on the photo, Figure 1. The typical droplet size was in the range of  $0.5\text{--}20\text{ }\mu\text{m}$  and strongly varied from sample to sample. An LC was aligned planarly in the droplets and they had a bipolar structure. LC droplet optical axes are chaotically distributed in the nonilluminated region. At the same time they are ordered in the illuminated region. The optical axes of LC droplets are predominantly alligned transversely to the polarization vector of UV light. We define this direction as a quasidirector  $d^*$  of oriented droplet systems.

The degree of LC droplet orientation can be described by order parameter  $S^*$  of their optical axes which we defined as in the case of the order parameters of LC.<sup>8</sup> It is sufficiently high ( $S^* \cong 0.7$ ) at room temperature and decreases monotonically with increasing temperature (Figure 2). If droplets don't interact with each other, the value  $S^*$  is determined by interaction between a droplet and a polymer matrix. In initial state this interaction produces the degenerate planar orientation of an LC and it leads to the bipolar structure of director distribution  $d(r)$  in the droplet volume. Anisotropy of the polymer matrix results in additional interaction between the LC at the droplet surface and the polymer matrix. We suppose that director distribution inside droplets doesn't change under UV-illumination and is described by vector

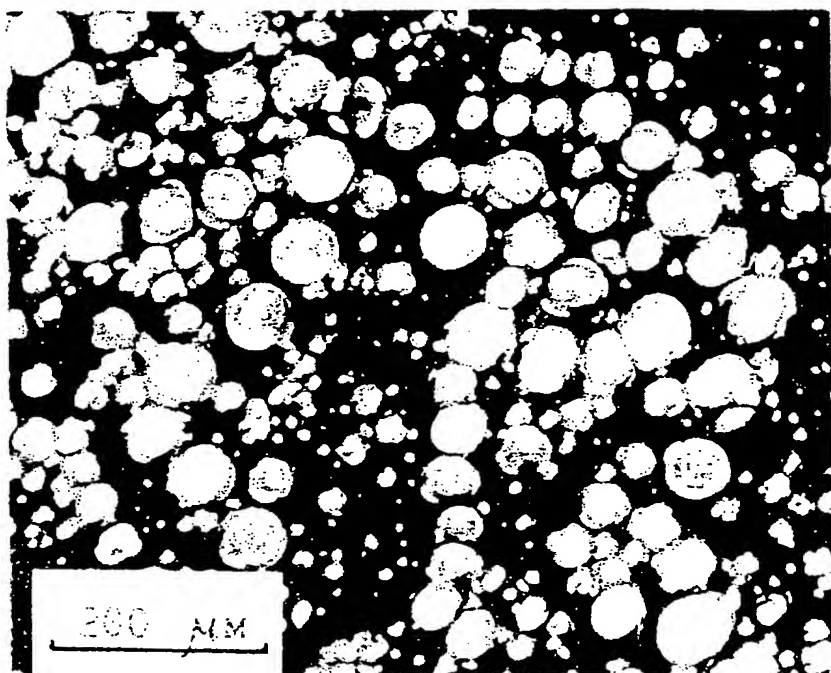


Figure 1 A photo of the liquid crystal dispersion in polymer.

$n \equiv (n_r, n_\theta, n_\phi) \equiv (0, 1, 0)$  in the spherical coordinate system with  $Oz$  axis along the droplet axis. If the interaction potential has the Rapini form, then  $U = W/2 \int (ne)^2 d\sigma$ , where  $W$  is anchoring energy,  $e$  is the unit vector along the anisotropy axis induced in the polymer. Integrating over the droplet surface yields  $U = 1/2 W + 4\pi R^2/3 + (1 + P_2(\cos\beta))$ , where  $\beta$  is an angle between the droplet axis and the direction of the anisotropy axis of a polymer matrix,  $P_2(x)$ -Legendre polynomial. Then for the order parameter  $S^*$  we have

$$S^* = \langle P_2(\cos\beta) \rangle = -1/2 + 3/4\alpha + (\exp(\alpha)/I(\alpha) - 1),$$

where  $I(\alpha) = \int_0^1 \exp(\alpha x^2) dx$ ,  $\alpha = W\pi R^2/kT$ . It is clear, that the temperature dependence  $S(T)$  is determined by ratio  $W/T$ . In particular, if  $S^* \cong 0.7$ ,  $R \cong 1 \mu\text{m}$ ,  $T = 300 \text{ K}$ , we can obtain a reasonable estimation for anchoring energy of  $W \cong 10^{-5} \text{ erg/cm}^2$ .

It should be noted, that a characteristic temperature  $T^* < T_c$  exists, where parameter  $S^*$  decreases sharply while no drastic change in the value of the matrix birefringence is observed (see Figure 2). This phenomenon is not clear and worth to be studied in future. Another reason for droplet axis orientational order may be their long distance interaction through a matrix. In this case the order parameter must depend strongly on the droplet concentration.

As is expected, light scattering in the obtained system depends dramatically on light polarization (see Figure 3), because of two main factors. First of all, the difference of refractive index  $n_m$  of a matrix and effective refractive index  $n$  of droplets depends on the  $E$ -vector direction. In our case, the magnitude of the  $n_m$  is close to the value of refractive index  $n^0$  for ordinary light beam while the difference between  $n_m$  and

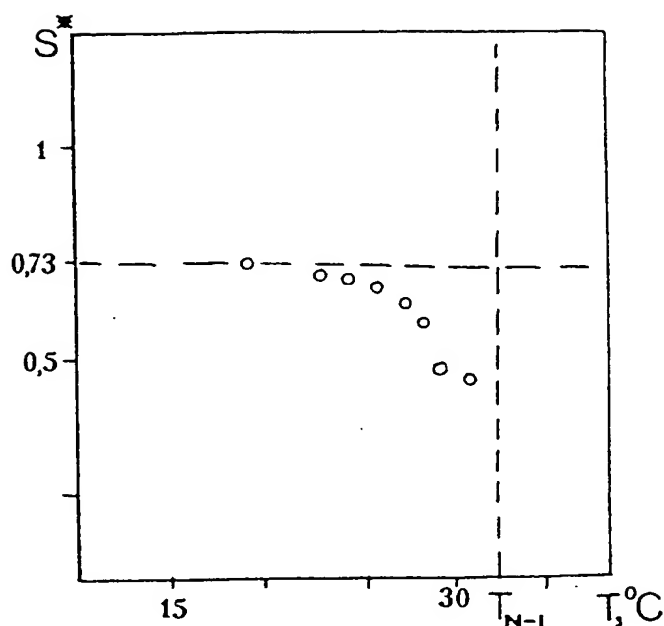


Figure 2 The temperature dependence of order parameter.

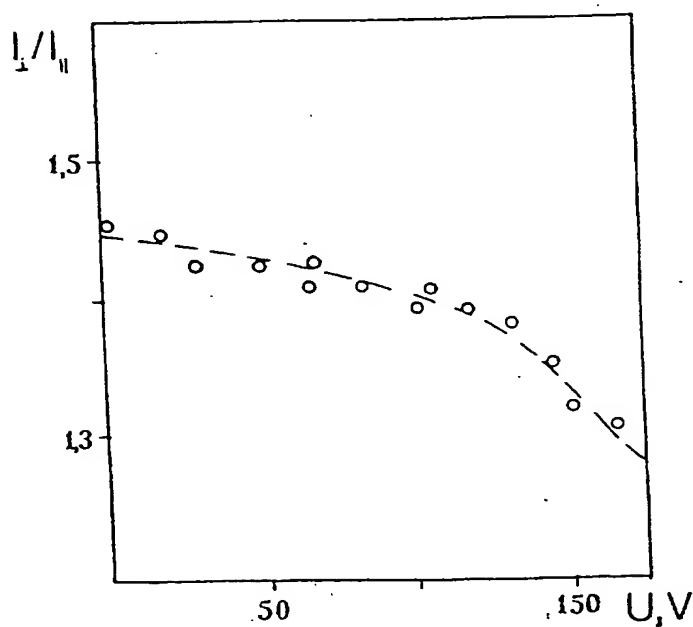


Figure 3 The dependence  $I_{\perp}/I_{\parallel}$  on  $U$ .

refractive index  $n^e$  for extraordinary beam is much more than  $n_m - n_o$ . Thus, light scattering for the polarization  $E^e \parallel d^*$  should be stronger than for  $E^o \parallel d^*$ .

The second factor is connected with a strong dependence of light scattering, caused by LC director fluctuation, on the vector  $E$  orientation. It is well known that ee-scattering is much stronger than oo- or oe-scattering.<sup>8</sup> Thus, the scattering of the

$E^*$  beam must be considerably stronger than that for the  $E^0$  beam. Hence, both the factors lead to the scattering greater for  $E^*$  polarization, as can be seen from Figure 3.

Under electric field, optical axes of droplets reorient normally to the glass plates, that is along the propagation of a light beam. The matching of  $n_m$  and  $n^*$  values and transparency for the e-polarized beam are improved with increasing voltage and the transparency for the o-beam virtually does not change. As a result, ratio  $I_{\perp}/I_{\parallel}$  is reduced with increasing voltage ( $I_{\perp}$  and  $I_{\parallel}$  are intensities of not scattered beams, passed through the cell and polarized along and transversely to the direction  $d^*$ , respectively, Figure 3).

It should be noted, that previous results concern the polarized light. If randomly polarized illumination was used, both scattered and transmitted beams became polarized.

## CONCLUSION

In conclusion, it was shown, that the effect of light-induced anisotropy can be successfully applied to control a mutual alignment of liquid crystal droplets in a polymer matrix. In our opinion, the proposed method is perspective for obtaining a stable orientation of droplets without stretching a matrix. As a result, not ellipsoidal, but quasispherical droplets have been produced. In addition, the method allows one to fabricate regions with different direction  $d^*$  in different areas of a dispersive film. It can be applied to optical information recording and observation of some interesting visual effects in PDLC-systems. One more fascinating feature of the proposed technique is a principal possibility to control parameter  $S^*$  and anchoring energy by a change in light intensity or exposure time.

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A TECHNIQUE TO ALIGN LIQUID CRYSTALS BASED ON  
BULK-INDUCED PHOTO-POLYMERIZATION

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p-1 1996  
p. 153-160 (8)

**Abstract** A technique based on bulk-induced alignment of liquid crystals by photo-polymerization to produce uniform planar and homeotropic orientation of liquid crystals is presented. The liquid crystal-photopolymer mixture is cured with linearly polarized UV-light in the isotropic phase. This technique obviates the need to give any special treatment to the bounding substrate and as such is independent of the nature of the substrate. This has given rise to possibilities of using liquid crystals for storing information with a high degree of spatial resolution of 10-20 $\mu$ m and has been used to generate patterned orientation of liquid crystals.

The homeotropic alignment in the smectic C phase has opened up new possibilities to make storage displays. The surface studies of the photopolymer aligned substrate with a Scanning Tunneling Microscope suggest that the surface modification dominates the alignment of liquid crystals.

INTRODUCTION

Uniform alignment of liquid crystals has been a subject of intensive research investigations during the last more than two decades. The subject is essential and interesting for both basic studies as well as for device applications. A variety of techniques have been developed and commercialized to produce uniform orientation of liquid crystals. Most of these techniques are based on surface modification of the substrate which can be produced by i) angular deposition of dielectric materials<sup>1</sup>, ii) thermal polymerization followed by buffing<sup>2</sup>, iii) organosilane coating<sup>3</sup>, iv) lecithin coating, v) photo-polymerization<sup>4-7</sup> etc. All these techniques are based on complex anisotropic surface anchoring interactions. Recently reported new techniques based

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on photo-polymerization have stimulated considerable research interests due to their unique feature in providing the capability to control and vary the macroscopic orientation direction of liquid crystal molecules locally within a plane. This has opened up new possibilities to make complex hybrid liquid crystal displays for data storage with a high degree of spatial resolution. We wish to report below a new modified technique to promote uniform planar and homeotropic orientation of liquid crystals based on bulk-induced photo-polymerization. This technique has been used to record patterns with a high degree of spatial resolution on liquid crystal cell without resorting to etching of the electrode patterns on the bounding substrate.

The homeotropic aligned smectic C cell by this technique has been shown to exhibit storage capability by application of appropriate low frequency electric field and subsequent heating to smectic A phase. The imaging of liquid crystal molecules adsorbed on surface of a photo-polymer aligned substrate with a Scanning Tunneling Microscope has revealed interesting results and strongly suggests that the surface modification dominates the alignment of liquid crystal molecules even in the present case.

### EXPERIMENTAL

Cleaned glass substrate without any previous surface treatment were used to make a liquid crystal cell. The cell thickness was controlled by glass/polymer spacers of a desired thickness (4-10  $\mu\text{m}$ ). A number of liquid crystal mixtures exhibiting nematic, smectic and chiral tilted smectic phases were used. A small amount (0.1-1.0% by wt.) of the photopolymer, poly-vinyl-methoxy cinnamate (PVMC) was added to the liquid crystal mixture and a uniform solution was made in chloroform which was subsequently allowed to evaporate completely. The mixture was filled into the sandwich cell in its isotropic phase. The cell was cured with linearly polarized UV-light ( $\lambda \sim 320\text{-}420\text{ nm}$ ) using a Xenon lamp or a metal halogen lamp. A Glan prism polarizer from Bernhard Halle, Berlin was used as a UV-linear polarizer. The light intensity was  $\sim 3\text{-}10\text{ mW/cm}^2$  and the curing time was 5-30 minutes. The cell temperature was maintained at  $> 10^\circ\text{C}$  above the clearing temperature during curing by an Instec Hot Stage. A Leitz polarizing microscope along with a photomultiplier setup and a digital storage oscilloscope were used to study the alignment and electro-optical properties of the aligned cells. Electrical signals were generated using a function generator (Hewlett-Packard 3312A) coupled with an amplifier (Krohn-Hite 7500).

The STM studies were performed with a commercial Nanoscope II (Digital Instruments, Inc.). The STM was operated in the constant current mode. The tunneling conditions were typically 0.2-1.0 nA (tunneling current) and 200-1500 mV (tip negative bias).



### RESULTS AND DISCUSSION

Well aligned planar cells could be obtained by curing the liquid crystal-photopolymer mixture with linearly polarized light well above its clearing point ( $> 10^{\circ}\text{C}$ ). The quality of the alignment was checked by rotating the cell between crossed polarizers and under a polarizing microscope. The preferred macroscopic orientation of the liquid crystal molecules in the nematic phase was determined by tilting the cell under a polarizing microscope between crossed polarizers. The tilting of the planar oriented cell results in birefringence, unless the director is aligned parallel to one of the polarizers and parallel to the tilting axis. The macroscopic orientation direction of the liquid crystal molecules is perpendicular to the polarization direction of the UV-light. The orientation direction is more easily identifiable in planar oriented smectic phases by the direction of the fan shaped texture. We could produce by this technique, uniformly aligned planar oriented cells using different liquid crystal mixtures exhibiting nematic, smectic and chiral smectic phases. The cell could be easily switched by appropriate voltage pulses in the nematic and chiral smectic C phases. The switching characteristics of the nematic cells prepared by photopolymerization and prepared by the conventional rubbing technique were quite similar. However, there was a lowering of the nematic-isotropic transition temperature by a few degrees by doping with photo-polymer. The electro-optical response of the LC cells in chiral tilted smectic phase ( $S_C^*$ ) prepared in this manner and in conventional manner were qualitatively identical. Figure 1(a,b) show the variation of the spontaneous polarization as a function of temperature and switching times as a function of voltage, respectively, of two cells containing ZLI-3654 mixture ( $K \rightarrow -30^{\circ}\text{C} \rightarrow S_C^* \rightarrow 62^{\circ}\text{C} \rightarrow S_A \rightarrow 76^{\circ}\text{C} \rightarrow \text{Ch} \rightarrow 86^{\circ}\text{C} \rightarrow \text{Iso}$ ) prepared by

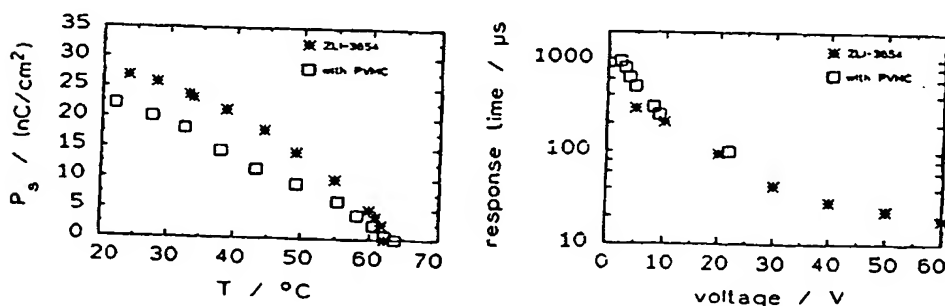


Figure 1(a) Variation of spontaneous polarization with temperature and (b) variation of switching time with applied voltage.

conventional surface alignment technique using a rubbed polyimide layer and by bulk-induced alignment using PVMC (0.8% by weight). The spontaneous polarization and the switching times are nearly identical in the two cases. Figures

2 & 3 show the variation of contrast ratio as a function of applied voltage and

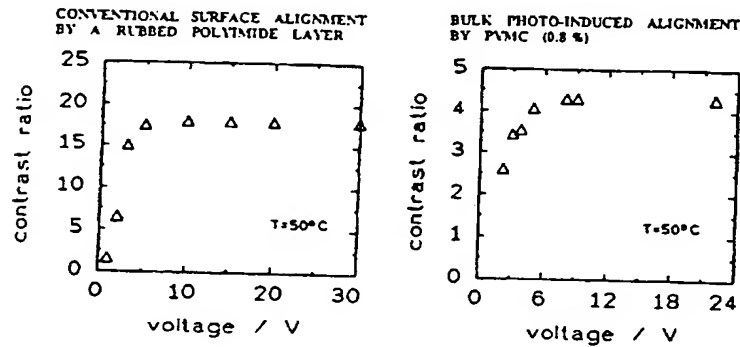


Figure 2 Variation of contrast ratio of polyimide rubbed cell and photo-polymer aligned cell containing ZLI-3654 mixture as a function of the applied voltage.

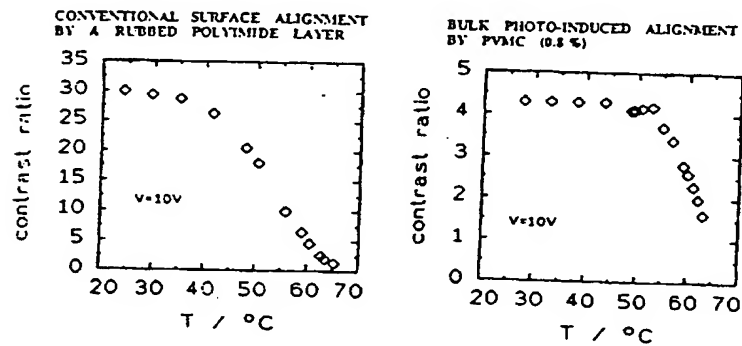


Figure 3 Variation of the contrast ratio of polyimide rubbed cell and photo-polymer aligned cell containing ZLI-3654 mixture as a function of temperature.

temperature for the above two cells. The contrast ratio is much lower in the cell prepared by photo-polymerization than the one prepared by conventional rubbing.

#### Pattern Storage By Bulk-induced Photopolymerization

This alignment technique has been used to store patterns optically on a liquid crystal cell. The pattern to be stored is made on a photomask. The nematic liquid crystal-polymer cell was exposed with linearly polarized UV-light through the photomask till the polymerization is complete. Subsequently, the polarizing prism was rotated through an angle of  $\pm 45^\circ$  and the cell was exposed with polarized UV-light through a complementary mask. The two portions of the cell have different macroscopic orientation direction of the liquid crystal molecules. The liquid crystals being birefringent, they produce optical contrast when viewed between appropriately oriented polarizers. Figure 4 shows one such pattern recorded by this technique. The



Figure 4 Photograph of a pattern stored optically on a liquid crystal cell by bulk-induced photopolymerization. See Color Plate IV.

spatial resolution could be as high as (  $10\text{-}30\mu\text{m}$  ) and the stored pattern has a long memory. Recorded patterns have not shown any visible decay for more than a year under ambient conditions. Memory test under extended UV-exposure has not been carried out so far. The pattern could also be recorded in a planar oriented liquid crystal cell filled with liquid crystal-polymer mixture by curing the cell with polarized light with its polarizing axis rotated through an angle of  $\pm 45^\circ$  with respect to the planar orientation direction.

#### HOMEOTROPIC ALIGNMENT

Uniformly aligned homeotropic cells could also be produced by bulk-induced photopolymerization. The homeotropic alignment was produced when the liquid crystal-photopolymer mixture was cured just a few degrees above the isotropic transition temperature of the nematic. The homeotropic cell appears dark between crossed polarizers and do not show any variation in transmission under rotation between them. The homeotropic alignment was also checked by rotating the cell under a polarizing microscope and with conoscopic investigations. Figure 4 shows

the micrographs of a homeotropically aligned cell containing liquid crystal mixture [ZLI-2711(PYP-709)80% + A-7(racemate)20%] and 0.5% PVMC with the following phase transition ( $K \rightarrow 43^\circ\text{C} \rightarrow S_C 54^\circ\text{C} \rightarrow S_A 58^\circ\text{C} \rightarrow N 66^\circ\text{C} \rightarrow I$ ) at  $53^\circ\text{C}$ .

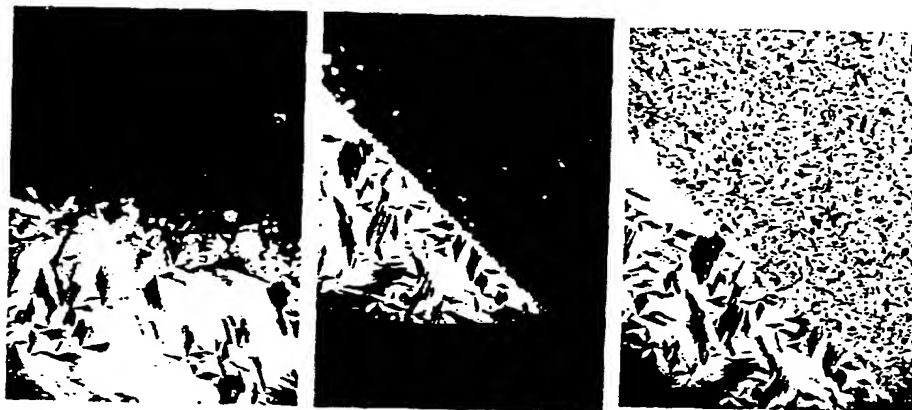


Figure 5 Micrographs of a homeotropically aligned cell in  $S_C$  phase:  $\phi =$  (a)  $0^\circ$ , (b)  $45^\circ$ , and (c) scattering state with electrical voltage (20V, 100 Hz). See Color Plate V.

#### Storage Effect

On application of a low frequency voltage signal in the  $S_C$  phase, the cell goes into a scattering state (Fig. 5c) and on voltage removal the scattering state persists. The scattering state returns to homeotropic state on heating into  $S_A$  phase and persists on cooling into  $S_C$  phase (Fig. 5b). This principle can be used to selectively energize the selected areas in to scattering state which persists even on field removal and the original state can be regained by heating the cell into the  $S_A$  phase. The detail experiments are underway.

#### ALIGNMENT MECHANISM

It was thought that the uniform alignment in the photo-polymerization based cell could arise due to formation of an anisotropic polymer net work in the bulk/ or by surface modification of the substrate by the photopolymer as reported by Schadt et al.<sup>4</sup> In order to elucidate on this, a planar oriented cell obtained by bulk-induced photo-polymerization was opened up and the glass substrate were cleaned carefully with a mild solvent while ensuring that their molecular structure was not disturbed or modified by cleaning. On re-assembling the cell with such a pair of glass plates and filling it with a pure liquid crystal mixture, produced uniformly aligned planar cell, which was identical to the bulk-induced planar cell. This procedure could be repeated several times. It is obvious, that the alignment in subsequently cleaned cells is caused by the surfaces of the substrates as the filled liquid crystal mixture does

not contain any photopolymer. The formation of the anisotropic polymer network in the bulk in the subsequent cell is ruled out. It was reasonable to conclude that an ultra thin layer of the anisotropic polymer network gets deposited on the glass substrate during photo-polymerization. To check on this hypothesis, the Scanning Tunneling Microscope studies were carried out.<sup>8</sup> A small amount of liquid crystal PCH-5 was transferred on one such conducting optically flat glass plate and was heated to isotropic transition temperature (55°C) for five minutes and then slowly cooled down to room temperature. A Pt-Ir tip was brought close to the liquid crystal and carefully driven into the tunneling range. The STM was operated in constant current mode.

The adsorbed liquid crystal molecules on the glass substrate were observed to form ordered arrays of molecules over large areas (Fig.6). The liquid crystal

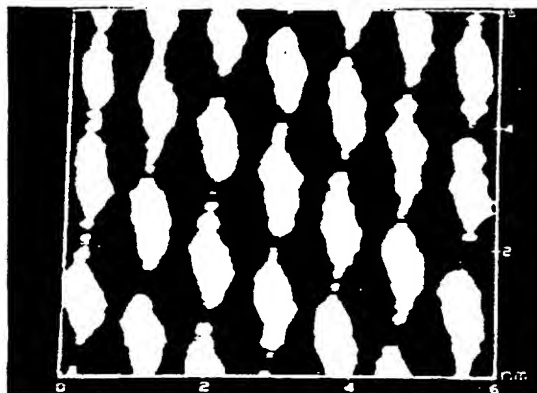


Figure 6

A 6\*6 nm STM image of PCH-5 molecules on indium oxide coated glass substrate with a ultra thin layer of PVMC deposited by bulk-induced photo-polymerization. See Color Plate VI.

molecules exhibit in addition to a long range orientational order, a high degree of positional order which is absent in the bulk.

The ordering of the liquid crystal molecules on the conducting glass substrate can be caused only by the anisotropic polymer net work on the glass surface. These studies lend support to the hypothesis that the surface modification of the substrate during photo-polymerization leads to the alignment of liquid crystal molecules.

### CONCLUSIONS

A new technique based on bulk-induced photopolymerization to produce planar and homeotropic alignment has been developed. The planar orientation technique has been used to store patterns optically with a high degree of spatial resolution. The homeotropically aligned cell in the  $S_C$  phase could give rise to new type of storage

displays. The subsequent planar cells obtained after cleaning the glass substrate and STM studies on them strongly suggest that even in the bulk-induced photopolymerization technique, the surface modifications dominate the alignment mechanism.

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